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Destroying Chemical Wastes in Commercial Scale Incinerators

TRW Defense and Space Systems Group, Redondo Beach, Calif

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1978

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DESTROYING CHEMICAL WASTES
IN COMMERCIAL-SCALE INCINERATORS
Phase II

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The report summarizes the results of a Phase II test program demonstrating the effectiveness of thermal destruction of industrial wastes in commercial scale facilities. Phase I was a study effort to select and match suitable wastes and destruction facilities, and to develop a set of detailed facility test plans. Phase II evaluated the environmental, technical, and economic feasibility of thermally destroying fourteen selected industrial wastes in seven different existing commercial scale processing facilities. Results indicated that each of the wastes tested can be thermally destroyed at high efficiencies. Separate detailed reports published for each facility test series conducted and the two-volume Phase I report are listed in the references.

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FOREWORD AND ACKNOWLEDGMENTS

This report summarizes the results of a Phase II test program demonstrating the effectiveness of thermal destruction of industrial wastes in commercial scale facilities. Phase I was a study effort to select and match suitable wastes and destruction facilities, and to develop a set of detailed facility test plans. The objective of these Phase II demonstration tests was to evaluate the environmental, technical, and economic feasibility of thermally destroying selected industrial wastes in different types of existing commercial scale processing facilities. Seven thermal destruction facilities and fourteen different industrial wastes were tested under the Phase II program.

Separate reports were also published for each facility test series conducted. These facility reports present in detail the equipment description, waste analysis, operational procedures, sampling techniques, analytical methods, emission data and cost information. The individual facility reports and the two-volume Phase I report are listed in the references.

Work described in this report was sponsored by the Environmental Protection Agency, Office of Solid Waste, under Contract No. 68-01-2966. The EPA Project Officer was Mr. John Schaum, later succeeded by Mr. Eugene Crumpler. The technical work reported here was accomplished by personnel of TRW Defense and Space Systems Group and Arthur D. Little, Inc. TRW was the prime contractor for this work and was supported by ADL in the role of a major subcontractor. The Project Manager for TRW was Mr. Birch Matthews. The ADL subcontract was managed by Mr. James Stevens. Key project personnel also included Dr. Robert Ottinger of TRW and Dr. John Funkhouser of ADL, members of the program core team and managers of the Phase I effort for their respective organizations.

Others who made significant contributions to the Phase II program, in addition to the authors of this report, were: Dr. Joan Berkowitz and Messrs. William Frazier, Kenneth Keyser, Gerald Sachs, and Clifford Summers of ADL; along with Dr. Ray Maddalone and Messrs. Maynard Cole, Jim Hom, Tom Hurst, Joe Kennedy, Larry Kraft, Herb Lindewall, Dave Moore, and Ward Wright of TRW. TRW and ADL are grateful to the personnel of each of the thermal destruction facilities mentioned in this report for their cooperation in conducting the field tests.

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1. SUMMARY, CONCLUSIONS, AND RECOMMENDATIONS

SUMMARY

Destruction or disposal of chemical wastes, many of which contain hazardous components, is a significant and growing problem in our society. With the passage by the Congress of the Safe Drinking Water Act (PL-93-523) and the Resource Conservation and Recovery Act (PL-94-580, known also as the Solid Waste Disposal Act), the U.S. Environmental Protection Agency was granted the authority to establish rules and regulations which affect the handling and treatment of chemical wastes. Consequently, the Office of Solid Waste instituted a number of programs to obtain technical and economic data on the effectiveness of various methods of solid waste disposal. It was recognized that the problems faced by industry in the development of chemical waste disposal methods were distinctly different from those encountered by municipalities in disposing of municipal solid wastes. Reviews of the types and quantities of these wastes being generated by industry along with assessments of the general capabilities of various disposal technologies indicated that the two leading generic disposal methods for chemical wastes would be 1) controlled land disposal and 2) thermal destruction.

To develop information on the effectiveness of a variety of thermal methods for destruction of chemical wastes, the EPA initiated a two-phase program (Contract No. 68-01-2966) with the team of TRW Defense and Space Systems Group and Arthur D. Little, Inc. The results of that program, during which seven different thermal destruction systems were tested and fourteen high priority chemical wastes were destroyed, are presented in this report.

Development of the Test Program

Phase I of this effort was devoted to (a) identifying, classifying and prioritizing candidate wastes for thermal destruction, (b) selection of facilities in which technically meaningful tests of thermal destruction could be carried out, and (c) development of a sampling and analysis strategy to be applied in the test program.

The wastes were distinguished by elemental composition into four classes. Priority rating for the chemical wastes was based on the product of a hazard rating and a quantity rating. One hundred and thirty potential chemical waste sources were identified and contacted concerning the availability of wastes. Fifty wastes were ranked as prime candidates for Phase II field testing.

Criteria for selection of types of thermal destruction systems were developed and applied to the seventy-five candidate facilities identified. The maturity of a given technology and its potential for future utilization in hazardous waste management were important criteria in the selection of 24 prime candidate facilities for Phase II tests.

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The wastes were matched to commercially available facilities with suitable operating characteristics and general procedures for conducting the tests were developed. The sampling and analysis strategy was designed to provide quantitative information on the efficiency of thermal destruction of the identified major chemical waste components. It also allowed survey analyses for detection and quantification of species other than identified waste components, such as products of partial degradation of the waste.

Scope of the Phase II Program

Nine types of thermal destruction systems were identified as being potential candidates for this program. Six of these types were tested in the field during the Phase II program. The six tested and the reasons for selection were:

- Liquid Injection Incineration (The Marquardt Company and Rollins Environmental Services, Inc.)
    - potential broad applicability
    - demonstrated performance
- Pyrolysis (Surface Combustion Division, Midland-Ross Corporation)
    - potential for resource recovery (primarily heat)
    - can handle solid and semi-solid wastes
- Cement Kiln Incineration (Chem-Trol supplied waste blends at St. Lawrence Cement Co.)
    - utilization of chlorinated hydrocarbon waste as both an energy and raw material source
- Fluidized Bed Incineration (Systems Technology, Inc.)
    - applicability to industrial wastes
    - ability to handle aqueous wastes with suspended solids
- Wet Air Oxidation (Zimpro, Inc.)
    - ability to destroy aqueous wastes with low energy contents
- Rotary Kiln Incineration (3M Company and Rollins Environmental Services, Inc.)
    - potential broad applicability
    - demonstrated performance
    - ability to handle a variety of physical forms of waste

The fourteen wastes ultimately selected for testing during the Phase II program are listed below and on the following page along with the type of facility to which they were assigned.

Organic Liquids

- Ethylene waste (carbon and hydrogen)--liquid injection
- Hexachlorocyclopentadiene waste (carbon and chlorine)--liquid injection

- Nitrochlorobenzene waste (carbon, hydrogen, oxygen, nitrogen and chlorine)--liquid injection

- Chlorinated aromatics (carbon, hydrogen and chlorine)--cement kiln

- Polychlorinated biphenyls (PCBs) (carbon, hydrogen and chlorine) --cement kiln

- Styrene waste (carbon, hydrogen and sulfur)--pyrolysis (assignment based on description of waste as tar not containing sulfur)

Aqueous Liquids

- Phenol waste (dissolved and suspended organics containing carbon, hydrogen and oxygen)--fluidized bed

- Methyl methacrylate waste (partially separable organic phase containing carbon, hydrogen and oxygen)--fluidized bed

- Coke plant waste (dissolved organics containing carbon, hydrogen and oxygen or nitrogen, plus ammonia and cyanide)--wet air oxidation

- Amiben® waste (dissolved organics containing carbon, hydrogen, oxygen, nitrogen and chlorine)--wet air oxidation

Sludges and Solids

- API Separator Bottoms (wet sludge -- organics containing carbon and hydrogen)--pyrolysis

- Polyvinyl chloride waste (wet solid -- organics containing carbon, hydrogen and chlorine)--rotary kiln

- Rubber waste (solid -- organics containing carbon and hydrogen) --pyrolysis

- PCBs in capacitors (whole and hammermilled waste capacitors -- organics containing carbon, hydrogen and chlorine)--rotary kiln

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The sampling and analysis approach developed for these tests involved collection of three distinct kinds of samples. A sampling train was devised that allowed collection of a three-hour time-averaged sample of the gaseous effluent from the combustion zone itself. The results of analyses of this sample provided the primary criteria for evaluating the effectiveness of thermal destruction in each test. The train used standard field-tested hardware as much as possible. A specially designed and fabricated quartz-lined water-cooled stainless steel probe was used to preserve sample integrity while withstanding combustion zone temperatures from 500°C to over 1000°C. A solid sorbent module was designed and incorporated into the sampling train for collection of moderately volatile organic species. The combustion zone samples were returned to the laboratory for chemical analyses. Specific quantitative techniques were used to search for known waste components, and survey techniques were used for qualitative and quantitative determination of other species present.

A second kind of sampling involved drawing a sample of combustion zone gas, via a ceramic probe and heat-traced line, to continuous instrumental analyzers for combustion process indicator species: oxygen, carbon dioxide, carbon monoxide, nitrogen oxides, and total hydrocarbons. These data were used to monitor the steady-state operation of the thermal destruction facility during the test.

The third kind of sampling was conventional sampling of all final effluents from the thermal destruction facility: stack gases, scrubber waters, and ash or solid residues. This was done to verify that the test program itself was environmentally acceptable.

An estimation of the cost associated with destruction of each waste in a facility of the type tested was prepared for each test.

Results of the Test Program

Of the fourteen wastes that were tested during the course of this program, thirteen were found to be destroyed effectively by the type of facility selected for their destruction, although alternative and sometimes better waste/facility matches are possible. The one waste/facility combination that did not provide effective destruction was the styrene waste/pyrolysis match, which had been based on an outdated description of the nature of the waste that did not fit the material received for testing.

The primary criterion for evaluating the thermal destruction of a particular waste was the amount of undegraded and/or partially degraded waste material that could be found in the effluent from the reaction zone of the facility. This quantity has been expressed as a destruction efficiency, DE, which is effectively normalized to reflect the rate of feed. Destruction efficiencies achieved in these tests are summarized in Table 1-1. A DE value is not listed for wastes tested in the pyrolysis facility because pyrolysis is a conversion process, not a destruction process.*

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*However, the combination of pyrolysis with a close-coupled heat recovery system would achieve high waste destruction efficiencies.

TABLE 1-1. DESTRUCTION EFFICIENCIES CALCULATED FROM PHASE II TEST RESULTS

Waste	Type of Facility	Destruction Efficiency (%)
Ethylene	Liquid Injection	> 99.999
Hexachlorocylo-pentadiene	"	> 99.999
Nitrochlorobenzene	"	> 99.999
Chlorinated Aromatics	Cement Kiln	≥ 99.989*
Polychlorinated Biphenyls	"	≥ 99.986*
Phenol	Fluidized Bed	> 99.999
Methyl Methacrylate	"	> 99.999
Coke Plant	Wet Air Oxidation	~90
Amiben®	"	~90
Polyvinyl Chloride	Rotary Kiln	≥ 99.996
PCBs in Capacitors (Hammermilled)	"	> 99.999

*Based on stack emissions, not combustion zone data (see Section 3.5.1)

The liquid injection incinerators were found to be significantly over 99.9 percent effective in destroying all three of the wastes tested. Very high destruction efficiencies were also found for the fluidized bed and rotary kiln incinerators. These two types would also accept wastes with a much greater range of physical properties than the liquid injection incinerator. The cement kiln facility testing indicated only slightly lower destruction efficiencies than were obtained for the destruction of other chlorinated organic wastes in liquid injection or rotary kiln incinerators.

The destruction efficiency for the wet air oxidation process was estimated at about 90 percent. As had been expected, the aqueous effluents contained residual organic material, which would require follow-on treatment of the aqueous effluent by physiochemical or biological processes.

Pyrolysis represents a special case. This process is designed to convert waste to a useful energy form. The average conversion of organic material in the solid waste feed to a more useful form in the pyrolyzer effluent was 70 percent for API waste and 80 to 90 percent for the rubber waste. Pyrolysis effluent gas from the styrene tests had a composition quite similar to that of the waste itself; no useful treatment was accomplished by pyrolysis of this liquid waste.

The only cases during the test program in which organic waste constituents were detected in the final facility effluents (stack gas, scrubber waters or solid residue), were in the pyrolysis tests and in the rotary kiln incineration of whole capacitors. The ash (or char) resulting from all of the pyrolyzer tests contained organic waste constituents in concentrations ranging from 0.01 to 30 percent. From the whole capacitor rotary kiln test, ppm levels of PCBs were detected in the solid residue. These species were not present in the residue when the capacitors were hammermilled prior to incineration.

Economics of Thermal Destruction

The costs associated with thermal destruction of chemical wastes are sensitive to a number of variables among which the principal ones are:

- Chemical and physical properties of the wastes.
- Energy content of the wastes.
- Control of emissions to the environment.
- Type of destruction facility.
- Capacity of the facility.
- Capital investment in the facility.

Therefore, the costs of thermal destruction for a unit quantity of a chemical waste will vary widely, as shown in Table 1-2. For these estimates, capital costs were based on recovery of capital at 10% interest over 10 years, which is typical of the financial considerations required for a commercial installation. Capital related charges are from thirty to sixty percent of total charges; however, where large direct operating costs for auxiliary fuel or chemicals to control air pollution are required, the capital related charges are proportionately less. For small capacity facilities, the labor charges often become the major costs.

Based on the costs estimated in this work, a number of general observations are useful. First, the estimated costs for thermal destruction are much greater than those presently incurred by land disposal; furthermore, it is expected that the future costs for disposal into controlled landfill, if permitted, would be lower than for thermal destruction. Consequently, thermal destruction should be utilized principally for those chemical wastes which contain hazardous compounds for which other methods of treatment or disposal are restricted either by regulations or special environmental considerations.

Experience indicates that wastes which contain only carbon, hydrogen and oxygen and which can be burned in power generation systems can be destroyed while recovering some of their energy content. These types of wastes may also be utilized for judicious blending with wastes having low energy contents, such as the highly chlorinated organics, in order to minimize the use of fossil fuel energy.

Because of the significant reductions in unit costs of thermal destruction achieved by large capacity facilities, and because the wastes from a single

TABLE 1-2. SUMMARY OF ESTIMATED COSTS OF THERMAL DESTRUCTION

Facility Type	Fluidized Bed		Wet Air Oxidation		Pyrolysis			
Waste	Methyl Methacrylate	Phenol	Coke Plant	Amiben	API Separator	Rubber Wastes		
Annual Destruction Capacity	13200 M^3	22800 M^3	700000 M^3	50000 M^3	300 MT	1000 MT	2000 MT	6000 MT
Estimated Capital Investment ($MM)	5.98	6.07	10.7	2.2	0.44	0.67	0.92	1.50
Estimated Direct Operating Costs	$119.60/$M^3$	$ 71.20/M^3	$ 5.80/M^3	$ 6.20/M^3	$498.30/MT	$345.10/MT	$171.70/MT	$ 49.60/MT
Estimated Caoital Costs	$122.40/$M^3$	$ 68.80/M^3	$ 4.20/M^3	$11.80/$M^3$	$395.70/MT	$180.90/MT	$124.30/MT	$ 67.40/MT
Total Estimated Costs	$242.00/$M^3$	$140.00/$M^3$	$10.00/$M^3$	$18.00/$M^3$	$894.00/MT	$526.00/MT	$296.00/MT	$117.00/MT

Facility Type	Rotary Kiln			Liquid Injection			
Waste	PCB/Capacitors	PVC		Ethylene	Hexachlorocyclopentadiene	Nitrochlorobenzene	
Annual Destruction Capacity	5000 MT	335 MT	6700 MT	15000 MT	4500 MT	13620 MT	4540 MT
Estimated Capital Investment ($MM)	3.65	1.30	7.80	1.82	1.63	1.25	2.82
Estimated Direct Operating Costs	$543.90/MT	$ 719.30/MT	$296.30/MT	$36.50/MT	$394.80/MT	$167.70/MT	$115.30/MT
Estimated Capital Costs	$197.10/MT	$1,067.70/MT	$285.70/MT	$32.50/MT	$ 97.20/MT	$ 74.30/MT	$167.70/MT
Total Estimated Costs	$741.00/MT	$1,767.00/MT	$582.00/MT	$69.00/MT	$492.00/MT	$242.00/MT	$283.00/MT

process manufacturing operation will often be less than the annual capacity of a conventional size thermal destruction system, it seems likely that the historical trend for operation of thermal destruction facilities will continue. That is, thermal destruction facilities will be operated either as a toll operation by a private firm or, if captively owned by a manufacturing company, will serve a manufacturing complex or group of plants in a limited geographical zone.

CONCLUSIONS

- Thermal destruction is a technically feasible and environmentally sound method for the treatment of industrial chemical wastes. Under well-controlled conditions, the effectiveness of destruction of chemical wastes can be expected to exceed 99.9 percent.
- Organic chemical wastes can be matched effectively with thermal methods of destruction if the physical characteristics and approximate chemical composition are known.
- The rotary kiln in conjunction with a liquid injection incinerator represents the most versatile combination for thermal destruction of a wide variety of waste types.
- The charges for capital related items often represent from one-third to one-half of the total costs incurred in thermal destruction of chemical wastes. Large scale and high utilization are therefore expected to lower thermal destruction unit costs.
- The cost of removing environmentally unacceptable products of combustion, such as hydrochloric acid or nitrogen oxides, from off-gas streams is often a significant factor in the costs of thermal destruction, representing up to one-fifth of total waste destruction costs.
- The cost of auxiliary fuel is a significant factor (as much as 20 to 40 percent) in the total costs of thermal destruction of a waste if fuel oil is used. To reduce operating costs, destruction facility operators normally utilize higher energy content wastes to provide heat for destruction of wastes requiring auxiliary fuel.
- The relatively high cost of thermal destruction will lead to the use of other, less costly, methods for waste disposal to the extent that the latter are acceptable to regulatory authorities.
- The sampling and analysis strategy developed for this program, including the specialized train for sampling the combustion zone, was found to be successful and appropriate for evaluating thermal destruction performance.

RECOMMENDATIONS

- There is no need for further tests of the feasibility of thermal destruction of hydrocarbon and chlorinated hydrocarbon wastes in liquid injection, fluidized bed, or rotary kiln incinerators.
- Tests should be carried out on thermal destruction of other classes of chemical wastes such as organic phosphates (pesticides), fluorinated organics, and organic orthosilicates. These are categories that are industrially important and that may exhibit behavior in thermal destruction systems significantly different than the wastes tested.
- Tests should be performed to evaluate the use of high energy content wastes as auxiliary fuel for destruction of wastes with low heat content. Blending of wastes for this purpose would minimize the use of expensive and scarce fuels; however, environmental problems may occur which were not identified during this test program.
- The sampling and analytical strategy developed and tested during this program was successful and should be utilized in future programs of this kind.
- Rotary kiln, liquid injection, and fluidized bed incinerators should be utilized because of their demonstrated broad applicability for chemical waste treatment.
- The utilization of cement kilns for the thermal destruction of chlorinated organic wastes should be given serious consideration as a proven means of resource recovery.
- Pyrolysis as a method of thermal destruction should only be considered in conjunction with a close-coupled energy recovery system such as a steam boiler, primarily for hard to handle solid or semi-solid wastes with high energy content.
- Wet air oxidation of chemical wastes in combination with efficient wastewater treatment systems should be considered only on a highly selective basis.
- The licensing and inspection of thermal destruction facilities treating chemical wastes are recommended to ensure adequacy of design and operating conditions.

2. INTRODUCTION AND BACKGROUND

During the past six years, a number of studies designed to determine the type, quantities and forms of chemical wastes, the classes and adequacy of chemical waste management methods, and the changes to be expected over the next ten years in the generation and treatment of these wastes have been sponsored by the Office of Solid Waste and the Solid and Hazardous Waste Research Laboratory of EPA. In these studies, a large number of industrial wastes containing organic constituents have been identified as being conducive to destruction by thermal means. Furthermore, in many cases, thermal destruction was determined to be the most environmentally acceptable method of disposal and in some cases would be the only adequate method of disposal. Subsequent to the initial studies, the advent of the energy crisis and the passage of the Resource Conservation and Recovery Act (Solid Waste Disposal Act) have created a situation in which increasing attention is being given to both recovery and disposal methods for chemical wastes. Consequently, more precise information on both the effectiveness and the cost of thermal destruction methods is necessary in order to determine if they are the most environmentally and economically acceptable procedures.

In order to establish the effectiveness of thermal destruction, several experimental programs were carried out with bench and pilot scale equipment. These programs included theoretical considerations on the molecular decomposition mechanism, followed by experimental attempts to confirm the decomposition mechanisms and degradation products at different conditions. The resulting data, determined under generally well-controlled conditions, have elucidated the behavior of a small number of selected wastes undergoing thermal destruction and have been useful in confirming or modifying the applicability of thermal destruction to specific wastes. The next logical step in assessing the applicability of thermal destruction methods to actual industrial wastes is to determine the operating conditions in commercial scale facilities for acceptable destruction of chemical wastes. Acceptability of thermal destruction methods should be based on 1) the effectiveness of controlling the emissions to the environment to an acceptable level, 2) the proven availability of equipment, and 3) cost. With this information, regulatory agencies have a firm basis for establishing guidelines and regulations which are technically, economically and environmentally realistic. Furthermore, the information should benefit both industry and regulatory agencies by describing specific thermal destruction technologies which appear acceptable in meeting guidelines or regulations while identifying any potential problems associated with those technologies.

In order to provide a broad assessment of the capabilities of commercially available thermal destruction facilities, the U.S. Environmental Protection Agency awarded a two-phase contract (EPA Contract No. 68-01-2966) to the team of TRW Defense and Space Systems Group and Arthur D. Little, Inc. The first phase (Phase I) was the development of an operational plan for selecting chemical wastes and thermal destruction facilities that could be

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tested for their capabilities to destroy chemical wastes containing hazardous components (References 1, 2). This encompassed:

- Classification, identification, prioritization and selection of wastes which provided a reasonable cross-section of currently generated industrial wastes with particular attention to quantities and hazardousness of the waste.
- Careful selection of facilities, chosen to be representative of the most advanced engineering methods of thermal destruction.
- Assignment of top priority wastes to specific facilities on the basis that the wastes could be expected to be destroyed effectively, the transportation and handling of the wastes would be feasible, and all facilities would be tested with at least one priority waste.

The second phase of work (Phase II) used the Phase I results and plan to carry out the waste destruction tests. This phase encompassed:

- Developing a testing and analytical protocol and outfitting a mobile laboratory for field testing.
- Obtaining wastes from generators and arranging for shipment to the thermal destruction facilities.
- Contracting with the operators of thermal destruction facilities for the tests.
- Preparing a detailed test and analytical program for each facility and carrying out the program at the thermal destruction facility.
- Analyzing samples in the laboratory and interpreting data.
- Preparing a report on each facility tested (References 3-9).

It is the purpose of this report to describe and discuss the Phase II program. In the following paragraphs of this section, the results of the Phase I study are briefly reviewed in order to provide an introduction to Phase II, which represented the major endeavors of the program.

2.1 PHASE I PROGRAM

Prioritization of Wastes

Since there were thousands of chemical wastes that might be considered for this program, it was necessary to develop a system which permitted an effective and logical selection of those wastes for which information on the effectiveness of thermal destruction would have the most widespread utility. A review of various classification procedures indicated that elemental composition and physical form were most pertinent. The grouping based on elemental composition led to 16 classes which, because most of the wastes fell into only three of these classes, were reorganized into four major waste classes as shown in Table 2-1 along with an example of a typical waste.

A prime reason for using this classification system was to provide a method for recognizing when sufficient wastes with similar combustion characteristics had been located. In addition, recognition of this similarity helped match specific wastes to individual facilities based on the need for pollution control equipment.

Having developed a system for placing all organic chemical wastes into four classes, it was necessary to develop criteria for prioritizing them both within and among these classes. Two criteria were developed with which to prioritize the candidate waste materials. These were:

- Hazard Rating (r_{max}) - A given compound or waste may have a number of values for which it is considered hazardous (flammability, oral toxicity, inhalation toxicity, carcinogenicity, etc.). For each hazardous value, four ratings were established with assigned values of 1, 10, 100 or 1000 — the higher the rating, the more hazardous the waste. In assigning a hazard rating to an individual waste with several hazardous values, the highest hazard rating was used irrespective of which hazardous value the rating represented.

- Quantity (Volume) Rating (Q) - Because the data on waste generation volumes are both sparse and, in many cases, of questionable accuracy, a volume ranking system was developed so that major differences between wastes could be recognized. For this, four ranges of waste generation volume were chosen. The ranges selected were over 45,400 metric tons/yr, 4,540 - 45,400 metric tons/yr, 454 - 4,540 metric tons/yr, and less than 454 metric tons/yr (100 M lb/yr, 10 to 100 M lb/yr, 1 to 10 M lb/yr and less than 1 M lb/yr). These volume ranges were assigned ratings of 1000, 100, 10 and 1, respectively. In addition, when no known quantity was found for a waste stream, a waste quantity rating of zero was assigned.

After hazard and quantity ratings were assigned to a waste, the priority category was determined by multiplying the two ratings together. Thus, priority category I is the highest with a $Q \times r_{max} = 10^6$, while in priority category VII, $Q \times r_{max} = 1$.

Concurrently with waste prioritization, potential sources of waste streams were obtained from published lists of chemical manufacturers (References 10, 11). One hundred and thirty potential waste sources were identified and contacted to learn whether they would be interested in supplying wastes suitable for Phase II testing. Finally, 50 wastes (which would be the prime candidates for the Phase II work) were selected and ranked. Their

TABLE 2-1. CANDIDATE WASTE CLASSES

Waste Class	Elemental Composition	Example
1	Carbon and hydrogen	Tars from production of styrene
	and/or	
	Carbon, hydrogen and oxygen	Off-specification phenol
2	Carbon, hydrogen and nitrogen	Solid residue from manufacture of aromatic amines
	and/or	
	Carbon, hydrogen, nitrogen and oxygen	TDI manufacture reactor tar bottoms
3	Carbon, hydrogen and chlorine	Vinyl chloride monomer manufacturing wastes
	and/or	
	Carbon, hydrogen, chlorine and oxygen	Phenolic tar from 2,4-D manufacture
4	Carbon, hydrogen chlorine and nitrogen	Nitrochlorobenzene manufacturing wastes
	Carbon, hydrogen and sulfur	Petroleum refining sour waste
	Carbon, hydrogen and fluorine	Fluorinated herbicide wastes
	Carbon, hydrogen and bromine	Ethylene bromide manufacturing waste
	Carbon, hydrogen and phosphorus	Malathion
	Carbon, hydrogen and silicon	Tetraethyl orthosilicate wastes
	Carbon, hydrogen and sodium	Refinery spent caustic

selection was based on: availability of waste, priority category, availability of known alternative waste disposal methods and the expected feasibility of destroying the waste by thermal methods. The distribution among priority categories for the selected 50 wastes is shown in Table 2-2. There were only six wastes found to be in the highest three priority categories. In Table 2-3, the 50 selected wastes are described in terms of chemical class, priority category and physical form.

TABLE 2-2. DISTRIBUTION OF 50 SELECTED WASTES BETWEEN PRIORITY CATEGORIES

Priority Category	$Q \times r_{max}$	Number of Waste Streams in Category
I	10^6	1
II	10^5	2
III	10^4	3
IV	10^3	18
V	10^2	13
VI	10	8
VII	1	5
		Total 50

Selection of Thermal Destruction Facilities

Considering all of the potentially feasible thermal destruction processes which were likely candidates for this program, a total of eight types were selected as having been developed to a point where reasonably good engineering information was available on the achievable ranges of operating conditions. These types were:

- Liquid injection incineration
- Multiple hearth incineration
- Rotary kiln incineration
- Catalytic combustion
- Molten salt pyrolysis/combustion
- Pyrolysis
- Fluidized bed incineration
- Wet air oxidation

TABLE 2-3. SUMMARY OF WASTE STREAMS SELECTED DURING PHASE I FOR PHASE II TESTING

Chemical Class	Number of Wastes	Priority Category	Physical form
H-C and H-C-O	1	II	1 liquid
	2	III	1 liquid, 1 solid
	5	IV	2 tars, 1 liquid, 2 sludges
	5	V	3 liquids, 1 tar, 1 solid
Total	13		6 liquids, 2 sludges, 3 tars, 2 solids
H-C-N and H-C-N-O	5	IV	1 liquid, 2 tars, 2 solid
	6	V	3 tars, 1 sludge, 1 viscous liquid, 1 semi-solid
	2	VI	1 tar, 1 liquid
Total	13		3 liquids, 1 sludge, 6 tars, 3 solids
H-C-Cl and H-C-Cl-O	1	I	1 liquid
	1	II	1 solid
	1	III	1 solid
	3	IV	2 liquids, 1 tar
	1	V	1 Tar
	2	VI	1 liquid, 1 tar
	1	VII	1 tar
Total	10		4 liquids, 4 tars, 2 solids
Other Wastes			
A. N and Cl containing wastes	2	IV	1 liquid, 1 tar
	1	VI	1 solid
B. Sulfur containing organics	1	VI	1 liquid
	2	VII	1 liquid, 1 tar
C. Fluorine containing organics	1	VII	1 liquid
D. Bromine containing organics	1	V	1 liquid
E. Phosphorus containing organics	1	VI	1 liquid
	1	VII	1 liquid
F. Silicon containing organics	1	VI	1 liquid
G. Mixture of organics and sodium salts or caustic	3	IV	3 liquids
Total	14		11 liquids, 2 tars, 1 solid

A list of 75 candidate facilities was developed and each was contacted to (1) obtain information on the characteristics of the facility and (2) determine possible interest in participating in this program. As a result of this preliminary review, 24 test sites were selected as candidates for the Phase II testing. Evaluation criteria applied to facilities during initial telephone contact and subsequent site visits were as follows:

- Potential for future in hazardous waste management
- Compatibility of waste form and expected thermal destruction characteristics with the facility capabilities
- Technical advantages and disadvantages of each type of facility for a specific waste
- Adequacy of air pollution control equipment
- Availability of adequate sampling points
- Adequacy of instrumentation and monitoring of operating conditions
- Safety equipment and procedures
- Willingness of the facility management to be associated with this study

Although all of these criteria were important in the decision process, other factors were considered such as potential for resource recovery, the ability to conduct a controlled test and the scale (size) of the facility. Emphasis was given to the latter consideration since the objective of Phase II was to evaluate thermal destruction characteristics of actual industrial wastes processed in commercially available facilities. Commercial scale facilities were not available for the multiple hearth, molten salt, wet air oxidation and pyrolysis methods. Consequently, pilot scale units used by equipment manufacturers to establish the desired basis for commercial units were chosen. From a total of 24 site visits, fourteen facilities were chosen for the purpose of developing the details necessary to establish the magnitude of the Phase II work. These facilities were then matched with wastes by comparing the facility capabilities and limitations with the waste characteristics. The waste-facility matching was primarily dependent upon consideration of the following waste characteristics:

- Physical form: gas, liquid, slurry, sludge or solid
- Temperature range required for destruction: above 1090°C (2000°F), 760-1090°C (1400° to 2000°F), 370-760°C (700° to 1400°F), or below 370°C (700°F).
- Effluent gases: primarily oxides of carbon, hydrogen, or nitrogen; but also halogen, sulfur, phosphorus, or volatile metal species.

- Ash: nonfusible, fusible, and/or metallic
- Heating value: above 5500 kcal/kg (10,000 Btu/lb), 2800-5500 kcal/kg (5,000 to 10,000 Btu/lb), or below 2800 kcal/kg (5,000 Btu/lb).

The results of assessing facility capabilities and matching with waste types are shown in Table 2-4. These facilities and wastes were the basis for establishing the program carried out in the Phase II work.

2.2 PHASE II PROGRAM

The program planned during the Phase I work was subjected to considerable revisions both prior to beginning the Phase II work and during the performance period. The first modification was a reduction in the magnitude of the program by EPA based on the estimated cost of a program to investigate the thermal destruction of 50 wastes in 14 different facilities. The initial directive for the Phase II work was to evaluate the following facilities with the wastes indicated.

1. The Marquardt Company
   a) Off-specification isoprene
   b) Hexachloropentadiene
2. General Electric Company
   a) Ethylene glycol manufacturing residues
   b) Perchloroethylene manufacturing still bottoms
3. Hyon Waste Management Services, Inc.
   a) PCBs in waste capacitors
   b) Nitrochlorobenzene tars
   c) Catch basin grease (nitrile pitch from manufacture of surface active agents)
4. Chem-trol Pollution Services, Inc.
   a) Waste blends of chlorinated hydrocarbons (destruction in cement kiln)
5. B.F. Goodrich
   a) Vinyl chloride monomer manufacturing wastes (dichloroethane and heavily chlorinated wastes that contain vinyl chloride)

TABLE 2-4. WASTE/FACILITY MATCHING SUMMARY

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Liquid Injection	Multiple Hearth	Rotary Kiln	Catalytic	Molten Salt	Pyrolysis	Fluidized Bed	Wet Air Oxidation
Marquardt Co. Van Nuys, Ca.	Eimco BSP Belmont, Ca.	Pollution Controls Shakopee, Minn.	B.F. Goodrich Calvert City, Ky.	Atomics International Canoga Park, Ca.	Surface Combustion Toledo, Ohio	Systems Technology Dayton, Ohio	Zimpro, Inc. Rothschild, Wisc.
Off-spec isoprene Hexachlorocyclopentadiene still bottoms Organophosphate pesticides (malathion) Waste from polymer polyol production (polymerization of styrene with acrylonitrile) Dodecyl mercaptan wastes Fluorinated herbicide waste	Reactor bottoms from PVC manufacture Aromatic amine residues Isophthalic acid and terephthalic acid still bottoms	Epichlorohydrin manufacturing wastes Steam still bottoms from aniline and alkylated phenol production Acrylonitrile manufacturing wastes Reactor tar bottoms from adiponitrile manufacture Phenolic tar from 2,4-D manufacture Chlorotoluene production wastes Phenylamine tar wastes	Vinyl chloride monomer manufacturing wastes - dichloroethane and heavy chlorinated hydrocarbon wastes that contain vinyl chloride	DNT/MNT mix waste from DNT production Dichloroaniline still bottoms Phenolic tar from MCPA manufacture	API separator bottoms Tars from production of styrene Rubber manufacturing waste sludge Tars from production of phthalic anhydride (xylene process)	Off-spec phenol Amiben® manufacture liquid wastes Carbaryl manufacture wastes Ethylene manufacturing wastes Wastes from toluene diamine (TDA) production from dinitrotoluene (DNT)	Coke plant wastes Petroleum refining sour wastes
General Electric Co. Pittsfield, Ma.		Hyon Waste Management Chicago, Ill.				Hazen Research Golden, Colo.	Resource Recovery Irvine, Ca.
Ethylene glycol manufacture residue Waste residues from alkyl benzene production Perchloroethylene manufacture still bottoms		PCB (polychlorinated biphenols) wastes in capacitors Evaporate residue from the cumene process for phenol manufacture Nitrochlorobenzene tars Catch basin grease, nitrile pitch from production of surface active agents TDI manufacture reactor tar bottoms Diphenylamine (DPA) manufacture reactor tar bottoms Mercaptobenzothiazale (MBT) tars				Tetraethyl orthosilicate wastes Organic wastes from pharmaceutical manufacture Organic peroxide manufacturing wastes (from dicumyl peroxide manufacture) Ethylene bromide manufacturing wastes Urethane manufacture wastes	Refinery spent caustic Dinitrophenol wastes from dye manufacture
Prenco Manufacturing Madison Heights, Mi.		Chem-Trol Pollution Services Model City, N.Y.					
Still bottom from acetaldehyde production and by-product recovery operation Alkyl and aryl sulfonic acid wastes		Chem-Trol proprietary blended waste (high chloride organics)					

6. Systems Technology Corporation
    a) Off-specification and waste phenols
    b) Amiben® manufacturing liquid wastes
7. Surface Combustion Division of Midland-Ross Corporation
    a) API separator bottoms
    b) Tars from production of styrene
    c) Rubber manufacturing waste sludge
8. Zimpro, Inc.
    a) Coke plant wastes
    b) Petroleum refining sour wastes

During the course of the Phase II program, a number of changes from the aforementioned plan were required. Among the most important were the following:

- The withdrawal of two facilities (General Electric and B.F. Goodrich) from the program because of corporate decisions involving scheduling and proprietary technology.

- The inability to obtain special permits for conducting tests with PCB wastes in the Chicago area (Hyon Waste Management).

- The composition of wastes was found to be considerably different from that anticipated in the Phase I work, thereby making certain wastes inappropriate for testing in the facility with which they had been matched. For example, the high inorganic solid content of the Amiben® wastes was expected to create problems in the fluidized bed incinerator at Systems Technology Corporation.

- The decreased availability of wastes with resource recovery potential. For example, high energy content wastes such as ethylene glycol still bottoms were being burned in steam generating equipment at the manufacturing site.

As a result of these problems, it was necessary to obtain new wastes and make arrangements to test at different facilities. As a consequence of these changes, seven thermal destruction installations were tested and data were obtained on the destruction of fourteen high priority chemical wastes. The thermal destruction facilities tested and the wastes destroyed at each facility are described briefly in Section 3.1, and in greater detail in Section 5.

3. PHASE II TEST PROGRAM AND RESULTS

This section describes the major aspects of the Phase II Test Program, in which seven different thermal destruction facilities were tested to determine their effectiveness in destroying fourteen high priority chemical wastes. The facilities and wastes tested are described briefly, along with the operational procedures, sampling and analysis methods, and environmental considerations which were common to all facility tests. Modifications of these general schemes were necessitated in some specific cases; those variations are discussed in the individual facility reports which are summarized in Section 5.

A summary of the results obtained during the test program is presented in this section. The data generated from the sampling and analysis effort have been interpreted in terms of the efficiency of destruction of the original hazardous waste components and in terms of any potential adverse environmental impacts due to partial degradation or hazardous trace components of the waste. In addition, considerable effort has been given to development of an internally consistent set of economic analyses based on the test program results. Estimates of capital investment and operating costs for treatment of each chemical waste in a facility similar to that tested have been prepared and are summarized in this section. The results presented here are discussed further in Section 4.

3.1 FACILITIES AND CHEMICAL WASTES TESTED

The criteria for selecting and for matching the particular types of facilities and chemical wastes were developed in Phase I of this program and have been reviewed in Section 2 of this report. Table 3-1 presents brief descriptions of the facilities that were actually tested during Phase II, and Table 3-2 shows comparable information about the wastes actually tested.

The information that was originally acquired from the waste stream generators, or other sources, concerning waste characteristics and composition was frequently incomplete. It was also recognized that waste compositions are highly variable. These factors are illustrated by comparison of some of the "expected" waste compositions presented in Table 3-2 with those of the actual wastes received for testing. The styrene waste, for example, was originally described as a tar, with only carbon and hydrogen as major components. The styrene waste received was a liquid containing 8% sulfur. Inquiry of the waste generator revealed that a process change had occurred. For these reasons, a "survey sample" of each particular waste tested was acquired from the prospective source a few months prior to testing. This sample was analyzed and the results used in designing each detailed facility test plan.

Despite this precaution, some wastes were found to exhibit unanticipated properties when received at the test site. In several cases, the waste variability had significant impacts on the process or engineering aspects of the test (e.g., waste feed difficulties caused by change in

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TABLE 3-1. BRIEF DESCRIPTIONS OF THE FACILITIES TESTED

Facility Tested	Facility Type	Comments and Constraints on Suitable Wastes	Wastes Tested
The Marquardt Company Van Nuys, Ca.	Liquid injection (With wet scrubber)	•200-240 liters/hr (50-60 gallons/hr) •$1.4x10^6$ kcal/hr ($5.5x10^6$ Btu/hr) •Temperatures up to 1650°C (3000°F) •Liquid waste with low particulate only	Ethylene waste Hexachlorocyclopentadiene (C-5,6) waste
Surface Combustion Division, Midland Ross Corp. Toledo, Ohio	Pyrolysis (With rich fume incinerator)	•90-180 Kg/hr (200-400 lb/hr) •$0.5x10^6$ kcal/hr ($2x10^6$ Btu/hr) •Temperatures up to 760°C (1400°F) •Solids, sludges, tars •Resource (heat) Recovery potential	Centrifuged API separator bottoms Styrene tars Rubber manufacturing wastes
Systems Technology, Inc. Franklin, Ohio	Fluidized bed (With wet scrubber)	•Up to 1360 liters/hr (340 gal/hr) •$15x10^6$ kcal/hr ($59x10^6$ Btu/hr) •Temperatures 600-810°C (1100-1500°F) •Liquids, slurries, powders	**Methyl methacrylate waste** Phenol waste
Zimpro, Inc. Rothschild, Wis.	Wet air oxidation	•20-400 liters/hr (5-100 gal/hr) •Temperatures 230-325°C (450-620°F) •Pressure up to $1.1 x10^4$ Kilopascals (1600 psig) •**Aqueous solutions**	Coke plant waste Amiben® manufacturing waste
3M Chemolite Incinerator System Cottage Grove, Minn.	Rotary kiln (with wet scrubber)	•$1.8x10^3$ kg/hr (4000 lb/hr) •$22.7x10^6$ kcal/hr ($90x10^6$ Btu/hr) •Temperatures 980-1090°C (1800-2000°F) •Pumpable liquids and drummed wastes	Polyvinyl chloride waste
Rollins Environmental Services, Inc. Deer Park, Texas	Rotary kiln and liquid injection incinerator (with wet scrubber)	•$28x10^6$ kcal/hr ($110x10^6$ Btu/hr) •Temperatures 1300-1500°C (2400-2700°F) •Pumpable liquids and drummed wastes	Kiln: Discarded capacitors containing **PCBs** (polychlorinated biphenyls) Liquid injection: Nitrochlorobenzene waste

TABLE 3-2. BRIEF DESCRIPTIONS OF THE WASTES DESTROYED IN PHASE II TESTS

Waste	Physical Characteristics	Chemical Composition	"Expected" Characteristics
Liquid Injection—The Marquardt Co. Ethylene waste	Liquid, low viscosity 10,000 Kcal/kg (18,000 Btu/lb)	89% C; 9% H; 1.3% S Unsaturated and aromatic hydrocarbons <0.01% Ash. metals <1 ppm	Water separable oil containing heavy polymeric oils with traces of aromatics liquid >5000 Kcal/kg (>10,000 Btu/lb)
Hexachlorocyclopentadiene waste	Liquid, moderate viscosity Suspended, waxy particulate 2400 Kcal/kg (4300 Btu/lb) Miscible with #2 fuel oil	77% Cl; 21% H; <1% H, N, and S mainly C_5Cl_6 and C_5Cl_8 0.04% Ash. Fe, Si, Al, Na, Ca at 10-100 ppm	Mixture of chlorinated toluenes, pentanes, and benzenes. Liquid >2800 Kcal/kg (>5000 Btu/lb)
Pyrolysis—Surface Combustion API separator bottoms	Sludge; 70% water 1390 Kcal/kg (2500 Btu/lb)	85% C; 12% H; 1.2% S; <1% N Unsaturated and aromatic hydrocarbons ~10% Ash. Zn, Cr, F, Pb at 200-1000 ppm	
Styrene waste	Liquid, moderate viscosity suspended particulate 8900 Kcal/kg (16,000 Btu/lb)	85% C; 8% S; 7% H; <1% N Aromatic hydrocarbons. Elemental sulfur <1% Ash. Zn, Cr, Pb at 0.1-2 ppm	Polymeric tar containing styrene and ethyl benzene tar. >2800 Kcal/kg (>5000 Btu/lb)
Rubber waste	Solid; 30% water 5500 Kcal/kg (9800 Btu/lb)	80% C; 10% H; <1% S, N Polymeric unsaturated and aromatic hydrocarbons 1-5% Ash. Cr, Pb, Zn, F at 20-150 ppm	Solid waste containing SBR rubber, and carbon black plus the usual salts, fatty acids, soaps, etc. Solids >2800 Kcal/kg (>5000 Btu/lb)
Fluidized Bed Combustion—Systems Technology, Inc. Methyl methacrylate waste	Liquid, low viscosity, 38% water Gritty sediment <1500 Kcal/kg (<2700 Btu/lb)	38% C; 9% H; <1% Cl, N, S methyl methacrylate (34%) and other oxygenated organics 2% Ash. Na, S, Ti, Al, Ca, Pb, Si, Mg, P at 50-300 ppm	
Phenol waste	Sludge, 86% water <1500 Kcal/kg (<2700 Btu/lb)	10.5% H; 6% C, <1% N, S, Cl Phenols and cresols. 5.5% Ash. S, Na, Fe, Ca, Si, Al, K, Mg, and P at >25 ppm	
Wet Air Oxidation—Zimpro Coke plant waste	Aqueous solution Dissolved solids <1% Small amt. particulate <55 Kcal/kg (100 Btu/lb)	Phenol and cresol, 800 ppm Amines, 25-50 ppm. COD, 5520 ppm NH_3, Cl^-, $SO_4^=$ at 2500-3500 ppm CN^-, 310 ppm; pH 9	
Amiben waste	Aqueous solution Dissolved solids 6-7% <55 Kcal/kg (100 Btu/lb)	Dichloronitrobenzoic acid, 20g/l COD, 30 g/l Cl^-, 6 g/l; pH 12 Sodium, 5%	
Rotary Kiln Incineration—3M Polyvinyl chloride	Sludge, 72% water 28% solids 740 Kcal/kg (1300 Btu/lb)	Vinyl chloride monomer, 220 ppm Solids - polyvinyl chloride 2% Ash. Low metals	PVC resins containing 100 to 300 ppm vinyl chloride monomer. Solid. >5000 Kcal/kg (>10,000 Btu)
Liquid Injection—Rollins Nitrochlorobenzene waste	Liquid, moderately viscous Variable amounts of crystalline particulate 5050 Kcal/kg (9100 Btu/lb)	46% C; 23% Cl; 9% N; 3% H Nitrochlorobenzene (95%) <1% Ash. mainly Ca, Fe, Mg. 200 ppm S	Heavy ends and tars from ortho-chloronitrobenzene vacuum distillation. Tar. >2800 Kcal/kg (>5000 Btu/lb)
Rotary Kiln—Rollins PCB waste capacitors	1. Whole capacitors 2. Hammermilled capacitors; Oily shredded paper and metal	Presumably same as shredded waste below. 29% organics, mostly PCBs 32% paper and plastics 39% ash	Waste containing PCBs and alpha methylstyrene in capacitors. Solid. <2800 Kcal/kg (<5000 Btu/lb)

physical form) and on the economics of waste destruction. Generally, however, it was found that destruction of the waste in the facility originally selected was still technically feasible.

3.2 FIELD TEST PROCEDURES

3.2.1 General Operating Procedures

A detailed facility test plan describing specific sampling and analysis procedures was prepared and was reviewed by EPA prior to each field test.

Detailed operating procedures, including both a test plan and a safety plan, were reviewed and approved prior to the commencement of each field test. Procedures and operating conditions were also recorded during each test. The detailed operating procedures varied from test to test but included the following steps:

- Prepare instruments and sampling equipment.
- Purge system by burning clean fuel for preset period.
- Activate on-line instruments.
- Initiate waste feed and allow system to stabilize.
- Collect combustion zone sample (3-hour) and stack gas sample. Collect other feed and effluent samples.
- Terminate waste feed and on-line gas analysis.

The safety plan for each field test included: provisions for briefing all personnel involved in the test on safety aspects; specification of personnel protection procedures required; and procedures for emergency termination of test and/or evacuation of area if necessary.

3.2.2 Selection of Operating Conditions

The operating temperatures and residence times for the incineration tests conducted are summarized in Table 3-3. The test program was designed so that waste destruction efficiency can be evaluated at several operating conditions for each waste. Target test conditions were determined in consultation with the facility operator. The general selection strategy was that the first test for each waste should be done at the most stringent attainable operating conditions (high temperature, long residence time), with subsequent tests using less severe conditions. It was generally true that the normal operating range of parameters for a particular facility was not exceptionally broad.

At the Marquardt liquid injection incineration facility, the ethylene manufacturing waste was burned at three combustion temperatures: 1350°C, 1535°C, and 1750°C, with corresponding residence times of 0.188 sec, 0.139 sec and 0.157 sec. The test results suggest that destruction of the ethylene waste was equally efficient at the lower combustion temperatures

TABLE 3-3. OPERATING CONDITIONS FOR WASTE DESTRUCTION

Waste	Incinerator	Temperature	Residence Time
Ethylene Waste	Liquid Injection	1349° - 1752°C	0.14 - 0.19 sec
Hexachlorocyclopentadiene Waste	Liquid Injection	1348° - 1378°C	0.17 - 0.18 sec
API Waste	Pyrolysis	760°C	12.5 min
Styrene Waste	Pyrolysis	650° - 760°C	12.5 min
Rubber Waste	Pyrolysis	760°C	15 min
Phenol Waste	Fluidized Bed	740° - 757°C	12 - 14 sec
Methyl methacrylate Waste	Fluidized Bed	774° - 788°C	12 sec
Coke Plant Waste	Wet air oxidation	279°C at 107 atm	1.15 hr
Amiben® Waste	Wet air oxidation	281°C at 107 atm	1 hr
PVC Waste	Rotary Kiln	870°C in primary combustion zone, 980°-1090°C in secondary combustion zone	2-3 sec
Hammermilled PCB Waste	Rotary Kiln	1252°C in kiln, 1331°C in afterburner	3.2 sec
Whole PCB waste	Rotary Kiln	1339°C in kiln, 1332°C in afterburner	3.08 sec
Nitrochlorobenzene Waste	Liquid Injection	1307° - 1332°C	2.3 sec
Chlorinated Hydrocarbon and PCB Wastes	Cement Kiln		5-10 sec

and slightly longer residence times. However, since the ethylene waste had a relatively high heating value, the more efficient method for destruction of the waste is to utilize a high waste feed rate and a low air/waste ratio corresponding to 30 percent excess air, which results in a higher combustion temperature. Thus there is no economic incentive to operate at lower combustion temperatures. In fact, the lower combustion temperatures, as the result of lower waste feed rates and higher air/waste ratios, would increase the cost of ethylene waste disposal. The hexachlorocyclopentadiene (C-5,6) waste, on the other hand, had a low heating value and would require the addition of supplementary fuel to provide the necessary temperature for waste destruction. In the tests conducted, the air and No. 2 oil feed rates were held constant at three No. 2 oil/C-5,6 waste ratios: 2:1, 1.5:1 and 1:1. The resulting combustion temperatures and residence times at these three waste/fuel ratios were almost identical at 1363° to 1378°C and 0.172 to 0.178 sec. The primary difference among the three tests was the increased C-5,6 waste feed at the lower No. 2 oil/C-5,6 waste feed ratios and the corresponding lower amount of excess air, since the air feed rate was held constant. The third test, conducted at an excess air of 41 percent, and with equally effective waste destruction, shows that No. 2 oil/C-5,6 waste feed ratios higher than 1:1 were not necessary. However, although even lower No. 2 oil/C-5,6 waste feed ratios could conceivably be used, the cost of supplementary fuel is not a significant factor in the total disposal cost for the C-5,6 waste. The additional savings in fuel cost by reducing the supplemental fuel requirement even further would only be marginal.

For the API separator bottom waste, the styrene waste and the rubber manufacturing waste tested at the pyrolysis facility of Surface Combustion, the original test program was to test each waste feed at several pyrolyzer temperatures and residence times. When the testing was actually conducted, however, it was necessary to use the maximum pyrolyzer temperature 760°C (1400°F) and the maximum hearth speed (3 revolutions per hour) in order to adequately destroy the wastes. The maximum hearth speed was essential in order to spread the wastes thinly enough on the hearth to allow their complete pyrolysis. The variable changed with each run was, therefore, the waste feed rate. The waste feed rate was varied to find the maximum feed rate consistent with an acceptable ash while operating at maximum temperature and minimum residence time. For the API waste, the test data indicate that the particular pyrolysis system used has an effective capacity of about 17 kg/hr (37 lb/hr). When the waste feed was increased to 25 kg/hr (55 lb/hr), the system appeared to be overloaded, resulting in decreased yield of volatile pyrolysis products and significantly increased yield of ash. For the styrene waste, the maximum feed rate was limited to 10 kg/hr (2.20 lb/hr) by the capacity of the rich fume incineration used as an afterburner. For the rubber manufacturing waste, the lower feed rate of 7.27 kg/hr (16 lb/hr) resulted in highest volatile hydrocarbons and lowest ash yield.

At the fluidized bed facility of Systech, two test conditions were evaluated with both the phenol and methyl methacrylate wastes. The bed temperature was in the 740°C (1364°F) to 788°C (1450°F) range, and the residence time was from 12 to 14 sec. These operating conditions are typical for fluidized bed waste destruction. Since both wastes had a high water content, a greater portion of the fuel requirement was for the evaporation of water. The lowering of the waste destruction temperature in the fluidized bed would not lead to substantial savings.

For the coke plant waste and Amiben® manufacturing waste tested at the wet air oxidation facility of Zimpro, the operating conditions were selected on the basis of batch laboratory oxidation tests performed in shaking autoclaves. The dependence of oxidation on temperature, reaction time, and catalyst addition was determined and the reaction conditions for the pilot runs were set on this basis. Oxidation conditions at 280°C (536°F), 107 atm pressure, and one-hour reaction time with catalyst present appeared optimum to achieve more than 90 percent reduction in COD for both wastes. Under these conditions, laboratory oxidation of the coke plant waste indicated that the destruction of cyanides and phenols was in excess of 99.5 percent, results that were later confirmed in the pilot plant tests. The normal operating temperatures in wet air oxidation processes range from 150°C (302°F) to 320°C (608°F) at corresponding pressures of 15 to 205 atm. The selected operating conditions were therefore within the typical operating range for wet air oxidation processes.

At 3M Company's Chemolite rotary kiln incineration system, the waste selected for testing was a PVC waste containing residual vinyl chloride monomer. The operating kiln temperature was 870°C (1600°F), and the temperature in the secondary combustion chamber was 980°C (1800°F) to 1090°C (2000°F). These temperatures were already relatively low for the destruction of hazardous wastes. The test data suggest that destruction of the PVC waste may have been marginally less efficient when combustion zone gas residence time was reduced from 3 to 2 seconds. Further reduction of the residence time requirement, however, may lead to incomplete destruction of the vinyl chloride monomer present in the PVC waste.

The Rollins incineration system consists of a rotary kiln and a liquid injection burner feeding a common afterburner. The PCB-containing capacitors were incinerated in the rotary kiln both as a hammermilled fluff and as whole capacitors. The PCB tests were performed at maximum incinerator temperatures and residence times to operate under conditions of maximum destruction effectiveness. For the hammermilled PCB waste, the test was conducted at a kiln flame temperature of 1252°C (2286°F), an afterburner gas temperature of 1331°C (2428°F), and a total residence time of 3.2 sec. The effective destruction of PCB suggests that perhaps lower kiln and afterburner temperatures and hence reduced fuel oil feed may be acceptable. For the whole PCB-containing capacitors, the test was conducted at a kiln flame temperature of 1339°C (2442°F), an afterburner gas temperature of 1332°C (2430°F), and a total residence time of 3.0 sec. In this case, however, the ash produced was found to contain PCB at 470 mg/kg ash, thus implying that longer residence time in the kiln may be required. The nitrochlorobenzene (NCB) waste was tested in the liquid injection burner at two waste feed conditions, with the addition of diesel fuel to improve the atomization process. The NCB/fuel oil mixture tested contained 20 percent by volume NCB, although a laboratory test at Rollins indicated that up to 50 percent by volume of the NCB waste could be dissolved in the diesel oil. The tests were conducted at combustion temperatures of 1307°C (2385°F) and 1332°C (2430°F), and a residence time of 2.3 sec. The effective destruction of the NCB waste indicates that higher NCB/fuel ratio should be considered. The NCB waste also had a relatively high heating value of 5050 kcal/kg (9100 Btu/lb), and mechanical atomizers could possibly be utilized to atomize the NCB waste properly for incineration without blending with diesel fuel.

3.3 SAMPLING AND ANALYSIS METHODS

The methods summarized here are discussed in more detail in the individual facility reports of this program (References 3-9).

3.3.1 Sampling Methods

Sampling methods used in the facility tests were chosen to cover four basic areas:

1) A representative waste feed sample was obtained for each waste by compositing a number of grab samples of the material actually tested.

2) Continuous on-line monitoring of combustion zone gas composition was done to determine and follow steady state conditions. Gases were drawn continuously from the hot zone through a ceramic probe, and then through a heated Teflon®* sample line to a specially equipped trailer containing the on-line instruments. The gas entered a gas conditioner system. The gas conditioner supplied a cool, dry, particulate-free sample to all of the analyzers except the hydrocarbon monitor which used an untreated sample. A heated Teflon® line carried a gas sample from a tee in the unconditioned sample line to the hydrocarbon analyzer. The monitoring instruments used are listed along with their operating ranges in Table 3-4.

3) A time-integrated sample of combustion zone gas was taken using the train shown schematically in Figure 3-1. This consisted of an EPA Method 5 train with the following significant modifications:

   - A stainless steel jacketed, water-cooled probe with a quartz liner was used.

   - Ultrahigh purity glass or quartz fiber filters were used.

   - A solid sorbent trap, designed to absorb the organic constituents in the sample gas stream, was located downstream of the heated filter and upstream of the first liquid impinger. The sorbent trap, with overall dimensions of 170 x 45 mm, contained ~40g of Amberlite XAD-2®** (cross-linked polystyrene beads with very large surface area). The trap was found to have a collection efficiency of greater than approximately 90 percent for compounds boiling above 190°C (i.e., C_{10} and higher hydrocarbons) and approximately 10 percent or less retention for compounds boiling below 60°C (Reference 12). Quantitative estimations of organic materials with boiling points below 190°C were provided by the on-line hydrocarbon analyzer previously described.

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*Registered trademark of E.I. du Pont de Nemours & Co., Inc.
**Registered trademark of Rohm and Haas Company.

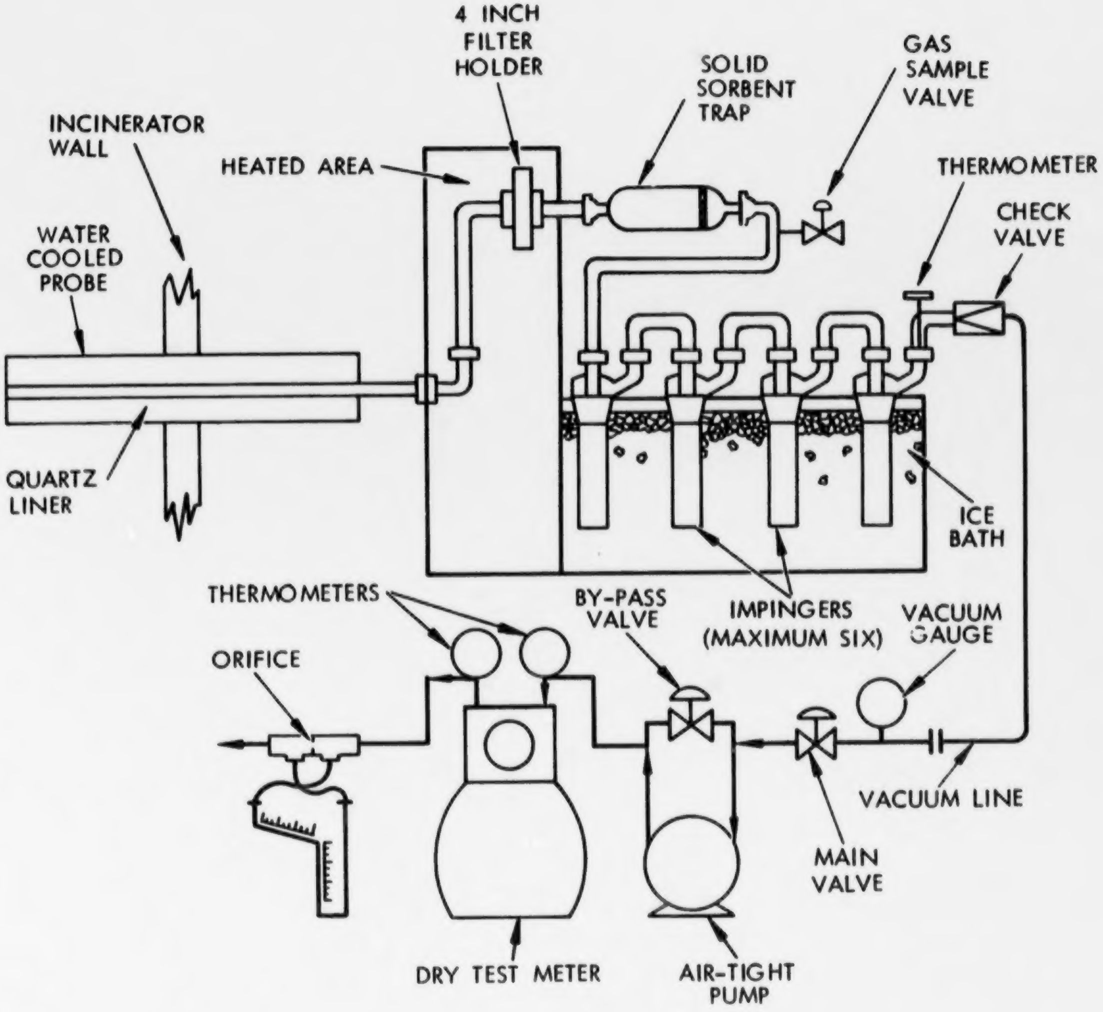
4 INCH FILTER HOLDER
SOLID SORBENT TRAP
GAS SAMPLE VALVE
INCINERATOR WALL
HEATED AREA
THERMOMETER
CHECK VALVE
WATER COOLED PROBE
QUARTZ LINER
ICE BATH
THERMOMETERS
BY-PASS VALVE
IMPINGERS (MAXIMUM SIX)
VACUUM GAUGE
ORIFICE
VACUUM LINE
MAIN VALVE
DRY TEST METER
AIR-TIGHT PUMP

Figure 3-1. Combustion Zone Sampling Train Schematic

TABLE 3-4. DESCRIPTION OF ON-LINE INSTRUMENTS

Species Analyzed	Manufacturer and Model	Range*
Total hydrocarbons (HC)	Beckman Model 402	0.05 ppm - 10% with eight ranges
Carbon monoxide (CO)	Beckman Model 865	2-200 ppm 10-100 ppm
Carbon dioxide (CO_2)	Beckman Model 864	0.05 - 5% 0.02 - 20%
Oxygen (O_2)	Taylor OA 273	0.05 - 5% 0.25 - 25% 1 - 100%
Oxides of nitrogen (NO_x)	Thermo Electron Model 10-A	0.05 - 10,000 ppm with eight ranges

*All of these manufacturers report an accuracy of ±1 percent of full scale for their instruments.

The combustion zone sampling train was operated at a flow rate of approximately 30 liters/min for three hours during each test. A second grab sample of combustion zone gas was collected in a sampling bulb/bag during each test for subsequent qualitative analysis of volatile species.

4) Samples of the stack effluent (EPA Method 5), fresh and spent scrubber waters and solid residue from the combustor (if any) were taken during each test to evaluate the environmental safety of the tests and ensure safe disposal of incinerator effluents.

3.3.2 Analysis Methods

Analyses of feed and effluent samples were designed to provide two types of information. One objective was to identify potentially hazardous components of the waste feed and search for those particular species in effluent samples. A second analytical strategy was to apply survey-type techniques to the effluent samples to detect other species of potential concern, such as partial combustion products and heavy metals. In analyses for identified waste components being sought in the effluent, the lower levels of concern were set by the detection limits of the various analytical techniques (see Table 3-5). These techniques were selected to allow detection of 0.001% or less of the major waste material components in the effluents. In the survey-type analyses, a concentration of 0.1 mg/cu m in the combustion zone effluent was established as the lower level of concern (Reference 1).

TABLE 3-5. SUMMARY OF CHEMICAL ANALYSIS METHODS

Method	Estimated Detection Limits for a Compound or Element Being Sought
Organic Analyses	
Gas Chromatography (GC)	∼1ppm in sample being examined
Infrared Spectrophotometry (IR)	∼3-5% of the sample being examined
Low Resolution Mass Spectrometry (LRMS)	∼10 μg (10% of a 100 μg sample)
Combined Gas Chromatography/Mass Spectrometry (GC/MS)	∼10 ng per μl of sample
Inorganic Analyses	
Inductively Coupled Plasma Optical Emission Spectrophotometry	∼0.5-2000 ppb
Spark Source Mass Spectrophotography (SSMS)	∼50-100 ppb
Atomic Absorption Spectrophotometry (AAS)	∼0.001 - 1 ppm

Prior to chemical analysis, particulate samples (from probe washes and filter catches) were dried and weighed. The combustion zone probe wash solids filters and solid sorbent traps, combustor solid residues, and those waste samples that were solid or semi-solid, were extracted with organic solvent(s) in continuous (Soxhlet-type) extraction devices. Scrubber water samples were subjected to separatory funnel liquid-liquid solvent extraction. Nonaqueous samples (particulate matter, solid residues and waste feed) were prepared for inorganic analysis by ashing or by continuous extraction with aqua regia. Portions of aqueous samples (scrubber water and impingers) were acidified and stored for inorganic analyses. Gas bulb/bag samples did not require treatment prior to analysis.

The analysis methods which were used for quantitative and qualitative analysis of the samples and sample extracts are summarized in Table 3-5. Portions of the organic extracts were also evaporated and analyzed gravimetrically to obtain quantitative estimates of total organic loadings.

Prior to each facility test, an analytical plan was published and approved which detailed the approach to be used. Each analytical plan took into account the unique aspects of the wastes and facility and tailored the analytical approach to fit the program needs.

3.4 ENVIRONMENTAL CONSIDERATIONS

In planning the Phase II test program, it was recognized that undesirable environmental problems could result during the implementation of these tests. The potential detrimental environmental effects were expected to result from: 1) transporting, storage, and handling of wastes prior to destruction; 2) emissions occurring during tests; and 3) disposal of liquid and solid residue remaining after destruction. Because of these environmental considerations, Phase II precautions were taken to avoid negative occurrences. These precautions are described in the following paragraphs.

3.4.1 Waste Transportation, Storage, and Handling

All wastes tested during this program were transported by licensed transit companies operating under the rules and regulations of the Department of Transportation. Waste storage areas at each facility were evaluated during site visits. Existing safety and handling procedures at each facility were also reviewed and modified, when necessary, for the specific waste to be tested. Spill prevention, containment, and cleanup procedures were included as part of a detailed test plan for each test series.

3.4.2 Test Emissions

Incomplete destruction of the wastes was considered a potential cause of hazardous emissions. Each test series utilized continuous monitoring of combustion gases for carbon monoxide and hydrocarbons as an indication of the completeness of combustion. In addition, every facility chosen for testing had air pollution control equipment, usually in the form of a wet scrubber. In the case of the pyrolysis tests, a rich fume incinerator was used to prevent emissions of unburned hydrocarbons. Stack emissions were also monitored during tests by using Bendix/Gastec analyzers to detect hazardous gaseous species.

3.4.3 Waste Residues

Residual material from some of the waste destruction tests included excess wastes, ash, scrubber water, or empty containers. Excess wastes were either destroyed on site at the conclusion of testing or sent to an approved landfill. Ash was also landfilled after analysis for waste constituents. Scrubber water was analyzed for harmful constituents and treated, if necessary, before discharge. Shipping containers, such as steel drums, were usually reclaimed by flushing with solvent; the solvent was then incinerated. In the case of the rotary kiln tests, both fiber and steel drums were fed into the kiln and incinerated.

3.5 TEST RESULTS

3.5.1 Waste Destruction Efficiencies

Thermal destruction of chemical wastes was the focus of this program. The primary criterion, therefore, for evaluating facility effectiveness was the amount of undegraded and/or partially degraded waste material that could be found in the effluent from the reaction zone (hot zone) of the thermal destruction facility.* This quantity has been expressed as a destruction efficiency, DE, which is effectively normalized to reflect the rate of waste feed. The calculated destruction efficiencies obtained from this test program are summarized in Table 1-1.

Destruction efficiencies of over 99.999 percent were attained for each of the ethylene and hexachlorocyclopentadiene waste tests conducted with the Marquardt liquid injection incinerator. No waste constituents were found in the reaction zone effluent above a minimum detection limit of 0.02 mg/cu m.

The effectiveness of a pyrolysis process is generally assessed in terms of percent conversion of the organic material in the feed to organic material in the vapor stream, since resource recovery is usually from the vapor stream while the ash or char is disposed of. For the three wastes tested in the Surface Combustion pyrolyzer, the average conversion of waste organic material to vapor stream organics was 70 percent for API waste, 60 percent for styrene waste, and 80 to 90 percent for rubber waste.

Combustion zone effluent samples were not taken at the Chem-Trol cement kiln by Ontario Research Foundation; therefore, the resulting minimum destruction efficiencies of 99.986 percent were calculated by ORF from input feed rates and stack emissions, and include potential removal of organics by the scrubber as well as combustion efficiency.

Fluidized bed destruction of phenol waste and methyl methacrylate in the Systech reactor resulted in destruction efficiencies of greater than 99.999 percent. No waste constituents were found in the effluent from the reaction zone. Detection limits were 0.03 mg/cu m for the phenol tests and 0.16 mg/cu m for the methyl methacrylate tests.

Wet air oxidation tests, as performed at Zimpro, produce both a gaseous and aqueous stream. The major portion of destruction products are expected to remain with the aqueous stream. Chemical compounds such as cyanides, phenols, and cresols in coke plant wastes were over 99 percent destroyed, while the Biological Oxygen Demand (BOD_5) and Chemical Oxygen Demand (COD) were reduced by about 90 percent. However, quinoline concentration was reduced by only 66 percent. For the Amiben® waste, over 99 percent of the dichloronitrobenzoic acid isomers were degraded to dichloronitrobenzene, while BOD_5 and COD were reduced by 90 and 82 percent, respectively.

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*Pyrolysis is the one exception.

Waste destruction efficiencies of over 99.999 percent were achieved for two of the three PVC waste tests with the 3M Company rotary kiln incinerator, and reaction zone effluents contained 0.02 mg/cu m of chlorinated organics. For the third PVC waste test combustion zone gas residence time was reduced from 3 seconds to 2 seconds. Waste constituents in the reaction zone effluents for this test were 0.04 mg/cu m, resulting in a calculated destruction efficiency of greater than 99.996 percent.

Destruction of PCB-containing capacitors in the Rollins rotary kiln resulted in an efficiency of over 99.999 percent for hammermilled capacitors. No waste was found in the reaction zone effluent at or above a detection limit of 0.1 mg/cu m. Whole capacitor tests left residual PCB in the ash of 470 mg/kg ash. No PCBs were detected in the reaction zone effluent for this whole capacitor test either. Assuming worst case, however, if one includes the PCB content in the ash waste, a destruction efficiency of 99.5 percent for the whole capacitor test results.

Nitrochlorobenzene wastes were destroyed in the Rollins liquid injection burner at an efficiency of over 99.999 percent. No waste constituents were found at or above a 0.05 mg/cu m detection limit in the reaction zone effluent from either of two NCB tests.

3.5.2 Chemical Characterization of Reaction Zone Effluents

In addition to determining the quantities of unaltered waste components, the test program was designed to include a search for potentially hazardous species emitted from the facility. It was the aim of this program to characterize the thermal destruction process, per se, independent of the particular pollution control system installed downstream. The survey mode analyses were conducted on samples collected from the hot zone of the facility, upstream of any scrubber, etc. [A few measurements, including particulate loadings, were made on the final gaseous and other effluents as well. (See 3.5.3).]

All of the chemical wastes selected for testing were considered to be potentially hazardous, primarily because of the organic components of the waste. Some wastes also contained substantial quantities of other species, such as heavy metals, that could lead to potentially hazardous emissions; these were sought in the effluent whenever found in the waste itself. Brief summaries of results of chemical characterization of hot zone effluents are presented below, with emphasis on those species which might be of concern in controlling emissions from a facility routinely destroying the particular waste.

For liquid injection incineration of the ethylene waste, no known toxic species were identified in the combustor effluent at levels that would require control technology. Sulfur dioxide was present at 100 to 200 ppm. For the hexachlorocyclopentadiene waste tested at the same facility, no known toxic organics were found. Hydrochloric acid emissions would, of course, require control. Other inorganics were lead, cobalt, chromium and manganese at 0.1 to 1.5 mg/cu m.

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For pyrolysis of both API waste and rubber waste, pyrolyzer gas effluent had a composition similar to that obtained from coking or gasification of coal. High levels of polynuclear aromatics (350-490 mg/cu m) and other condensable organics ($>$ 1% by volume) would require close-coupled, carefully designed heat recovery systems. Sulfur gases were present at $<$ 200 mg/cu m as S; lead and zinc were found for API waste only. Pyrolysis gas from styrene tests had a composition quite similar to the feed, but with more polynuclear aromatics; substantial quantities of soot were also formed.

Fluidized bed combustion of methyl methacrylate waste produced no known toxic organics in the combustor effluent. Lead was found at about 1 mg/cu m. A very similar composition was found for combustion of phenol at the same facility, except that lead levels were as high as 5 mg/cu m.

The aqueous effluents from wet air oxidation of coke plant waste and Amiben® waste contained residual organic material. For coke plant waste, identified species were phenol (1 mg/liter) and quinoline (13 mg/liter); COD was 500 mg/liter. These levels are probably acceptable for discharge to wastewater treatment. For Amiben® waste, dinitrochlorobenzene at 2 g/liter would require removal in a separate operation following wet air oxidation. Total COD for that effluent was 3 g/liter. Total volatile hydrocarbons in the vent gas were 180 ppm and 750 ppm for coke plant waste and Amiben® waste, respectively.

Rotary kiln incineration both of PVC waste and No. 2 fuel oil (background) test) at 3M Company produced polynuclear aromatic hydrocarbons at 2 to 5 mg/cu m in the hot zone effluent. Hydrochloric acid emissions were about 1.5 g/cu m and would, of course, require controls. Rotary kiln incineration of both whole and hammermilled PCB-containing capacitors did not lead to detectable amounts of toxic organic species in gaseous combustor effluent. Hydrochloric acid emissions were in the 450 to 700 ppm range. Potentially hazardous metals found were 11 to 12 mg/cu m of lead and 1 to 2.6 mg/cu m of tin.

Destruction of nitrochlorobenzene waste in a liquid injection incinerator (Rollins) did not result in formation of detectable quantities or organic materials known to be hazardous. Hydrochloric acid emissions from the combustor were 2.5 to 6 g/cu m and would certainly require emission controls.

3.5.3 Final Emissions - Stack, Scrubber Water, Ash

Final emissions from each waste destruction test (including exhaust stack gases, used scrubber water, and solid residues--ash) were sampled and analyzed to insure that no detrimental environmental effects resulted from any of the tests. Table 3-6 summarizes the final emissions measured at each facility for the wastes destroyed.

Stack particulate emissions ranged from 3 mg/m^3 for the Zimpro wet air oxidation tests to over 1,000 mg/m^3 for the Systech fluidized bed tests. Only the Systech tests significantly exceed the EPA Standards of Performance for Incinerators (Reference 13) limiting particulate emissions

TABLE 3-6. SUMMARY OF FINAL EMISSIONS

Facility and Type	Wastes Tested	Particulate in Stack (mg/m^3)	Scrubber Water Quality	Solid Residue Quality
Marquardt Liquid Injection	Ethylene	20-25	No organic waste constituents; metals <0.1 ppm	97-99% carbon; ≤0.2% organic waste constituents
	C-5,6	36-113	No organic waste constituents; metals ≤0.5 ppm	89-98% carbon; no organic waste constituents
Surface Combustion Pyrolysis	API separator bottoms	23-88	N/A	85% inorganic; alkyl substituted aromatics and aromatic waste constituents
	Styrene	28-43	N/A	96% inorganic; organic waste constituents and some PAHs
	Rubber	9-14	N/A	80% inorganic; high molecular weight aromatic waste constituents
Chem-Trol Cement Kiln	Chlorinated aromatic hydrocarbon blend	196	N/A	>99% inorganic; no organic waste constituents
	Above blend with PCBs	178	N/A	>99% inorganic; no organic waste constituents
Systems Technology Fluidized Bed	Phenol	1280-1430	No organic waste constituents; no significant metals	No organic waste constituents in bed sand
	Methyl methacrylate	560-630	No organic waste constituents; no significant metals	No organic waste constituents in bed sand
Zimpro Wet Air Oxidation	Coke plant	3	Phenol -1 mg/l; BOD-23 mg/l; COD-481 mg/l; quinoline-13 mg/l; Cu-250 mg/l; NH_3-2410 mg/l	N/A
	Amiben®	11	2,5 dichloronitrobenzene-2 g/l; BOD-5.3 mg/l; COD-30.5 mg/l; Cu-300 mg/l	N/A
3M Rotary Kiln	Polyvinyl chloride	71	No organic waste constituents; 480-800 mg/l Cl^-	N/A
Rollins Rotary Kiln	PCB-containing capacitors, Hammermilled	35	No organic waste constituents; <3 mg/l Cu, Fe, Pb, Zn, Al	No organic waste constituents
	Whole Capacitors	53	No organic waste constituents; <7 mg/l Cu, Fe, Pb, Zn, Al	~500 ppm PCBs
Rollins Liquid Injection	Nitrochlorobenzene	14-16	No organic waste constituents; Cl^--0.2%; NO_3^- - 60 mg/l	N/A

to 180 mg/m^3. However, most of the particulate from the Systech tests consisted of fine sand particles disintegrated from the fluidized bed by injection of high water content wastes through a single nozzle directly into the bed.

Scrubber water effluents resulting from these thermal destruction tests generally contained very little organic material, due to the high waste destruction efficiencies obtained. No organic waste constituents or other hazardous organics were found in the scrubber water samples at detection limits that usually ranged from 0.1 to 0.5 ppm. The one exception to this was the Zimpro facility, at which the aqueous effluent was not from a wet scrubber but was the media of the wet air oxidation process. In the Zimpro tests, certain waste constituents that were more resistant to wet air oxidation remained in the aqueous media at low concentrations. The wet air oxidation tests were also the only ones which resulted in a high metal content due to the copper catalyst added to the aqueous media.

In general, the wastes tested in this program had very low inorganic content and did not result in producing high metal concentrations in the wet scrubber effluents. Test burns of highly chlorinated hydrocarbons which required the addition of some form of caustic to the wet scrubbers resulted in increased levels of Na and/or Ca and Cl^- to the scrubber effluent.

The nature of the solid residues (ash) was unique to each facility. At Marquardt, a coke-like residue formed on the injector nozzles during the waste burns. The residue was almost entirely elemental carbon and, from the ethylene waste tests only, contained traces of uncombusted waste constituents. At Surface Combustion, as the wastes were pyrolyzed in the rotary hearth, a residue was left that consisted of virtually all the inorganics from the wastes plus primarily aromatic waste constitutents that were resistant to pyrolysis. Traces of polynuclear aromatic hydrocarbons (PAHs) were also found in the pyrolysis residues.

In the St. Lawrence Cement Company's burns of Chem-Trol waste blends and in the Systems Technology tests, the solid residues were not effluents of the facility's process. At St. Lawrence Cement, the solid residue produced by the kiln is mixed with gypsum to form the cement product. Thus the only important thing to note is that there were no organic waste constituents extractable from the kiln product. At Systems Technology, the solid residue is left in the sand bed of the fluidized bed reactor. Under normal operating conditions, this sand is not drained or disposed of. Here again, there were no organic waste constituents found in the sand.

At Rollins, the PCB-containing capacitors tested had an ∼40% ash content. This inorganic material was left as a solid residue in the rotary kiln. The residue from burning hammermilled capacitors did not contain any detectable PCBs (< 1 ppm). However, the residue from burning whole capacitors contained at least 500 ppm of PCBs.

3.6 ECONOMICS OF THERMAL DESTRUCTION

Although the results of this test program show that thermal destruction methods can be extremely effective in destroying certain types of chemical wastes, it is important to recognize that the cost of thermal destruction for chemical wastes can vary widely. The cost depends especially upon the type of facility required to handle the waste which determines the capital investments, the cost of energy (e.g., as auxiliary fuel) and the cost to control emissions (e.g., the removal of hydrogen chloride from effluent gases). Therefore, estimates of capital investments and operating costs were prepared for each of the facility types. These estimates were based on information provided by the facility operators and supplemented as appropriate by the application of generally accepted engineering factors. The estimated capital investments and operating costs shown in Tables 3-7 through 3-10 have been condensed from the individual facility reports.

All capital investments are for a base period of March 1976 at which time the value of the Marshall & Swift (M&S) index was 460. The capital investment estimates were in most cases based upon appropriate engineering estimates of purchased equipment costs to which generally applicable engineering factors for installation, buildings, instrumentation, engineering, construction and contingencies were applied. Capital investment estimates assumed a battery limits plant (e.g., no provisions were made for the installation of utilities such as steam generating equipment, electrical power substations, cooling towers and so on). Also, the capital estimates do not include any costs for the acquisition of land.

Variable costs were based on estimated quantities of fuel, electric power, cooling water and chemicals. Direct operating labor estimates were based on either the observed labor forces at the test facilities or upon experience with similar facilities. Appropriate factors for direct supervision, fringe benefits and plant overheads were applied to the direct labor estimates. Direct labor rates varied between approximately \$5.00 and \$8.00 per hour depending upon the labor classification. Unit costs for chemicals were taken as typical of the quoted delivered cost for the year 1976 in the Chemical Marketing Reporter. Maintenance labor and material was taken as a fraction of total capital investment. Unit cost for other variables was as follows:

• Fuel (oil or gas)	\$7.93/million kcal (\$2.00/million Btu)
• Electricity	\$0.015/kwh
• Cooling water	\$0.008/cu. meters (\$0.03/thousand gallons)
• Steam	\$8.80/metric ton (\$4.00/1000 lbs)

Annual fixed costs were taken as 27 percent of total capital investments. These were based on the assumption that the interest on borrowed capital would be 10 percent, depreciation would be 15% per year and that taxes and insurance would be 2% per year. Regardless of the approaches taken to analyzing the costs of capital, it is believed that from one-quarter to one-third of the capital investment must be charged annually if a thermal destruction system were operated as an economic enterprise.

TABLE 3-7. ESTIMATED CAPITAL INVESTMENT AND OPERATING COSTS FOR FLUIDIZED BED COMBUSTION AND WET AIR OXIDATION OF WASTES USED IN PHASE II TESTS

	Fluidized Bed Systech		Wet Air Oxidation Zimpro	
	Methyl Methacrylate Waste	Phenol Waste	Coke Plant Waste	Amiben® Waste
	13,200 cu m/yr	22,800 cu m/yr	700,000 cu m/yr	50,000 cu m/yr
Estimated Capital Investment, millions of dollars	5.98	6.07	10.7	2.20
Estimated Operating Costs, dollars per cubic meter				
Operating Labor	9.30	6.60	0.35	2.50
Auxiliary Fuel	35.70	37.00	1.00	0.50
Utilities, Chemicals, and Freight	38.30	6.30	0.50	1.20
Maintenance	36.30	21.30	0.60	1.80
Cost of Follow-on Treatment			3.30	0.30
Capital Related Items	122.40	68.80	4.20	11.80
Total Estimated Operating Cost, dollars per cubic meter	242.00	140.00	10.00	18.00

TABLE 3-8. ESTIMATED CAPITAL INVESTMENT AND OPERATING COSTS FOR PYROLYSIS OF WASTES USED IN PHASE II TESTS*

	Surface Combustion Division of Midland - Ross Corp.			
	API Separator Waste	Rubber Waste		
	300 Metric Tons/yr	1000 Metric Tons/yr	2000 Metric Tons/yr	6000 Metric Tons/yr
Estimated Capital Investment, millions of dollars	0.44	0.67	0.92	1.50
Estimated Operating Costs, dollars per metric ton				
Operating Labor	373.10	312.90	156.30	52.10
Auxiliary Fuel	52.80	21.10	21.10	21.10
Utilities, Chemicals, and Freight	5.80	5.60	5.60	4.50
Maintenance	117.30	53.60	36.80	20.00
Credit for Recovered Heat	(50.70)	(48.10)	(48.10)	(48.10)
Capital Related Items	395.70	180.90	124.30	67.40
Total Estimated Operating Cost, dollars per metric ton	894.00	526.00	296.00	117.00

*No estimate was prepared for pyrolysis of styrene tars, since pyrolysis of this waste was not found to be a technically feasible destruction method.

TABLE 3-9. ESTIMATED CAPITAL INVESTMENT AND OPERATING COSTS FOR LIQUID INJECTION INCINERATION OF WASTES USED IN PHASE II TESTS

	The Marquardt Company		Rollins Environmental Services	
	Ethylene Waste	Hexachlorocyclopentadiene Waste	Nitrochlorobenzene Waste	
	15,000 metric tons/yr	4500 metric tons/yr	4540 metric tons/4 mos	4540 metric tons/yr
Estimated Capital Investment, millions of dollars	1.82	1.63	1.25[*]	2.82[**]
Estimated Operating Costs, dollars per metric ton				
Operating Labor	20.60	69.50	29.10	46.00
Auxiliary Fuel	—	94.00	51.70	20.20
Utilities, Chemicals, and Freight	5.90	201.30	62.10	18.10
Maintenance	9.70	30.00	24.80	31.00
Capital Related Items	32.50	97.20	74.30	167.70
Total Estimated Operating Cost, dollars per metric ton	69.00	492.00	242.00	283.00

[*] Pro-rated investment for one-third time use of large facility.

[**] Based on engineering estimates of a facility dedicated only to destruction of nitrochlorobenzene wastes.

TABLE 3-10. ESTIMATED CAPITAL INVESTMENT AND OPERATING COSTS FOR ROTARY KILN COMBUSTION OF WASTES USED IN PHASE II TESTS

	Rollins Environmental Services	3M Company	
	PCB Capacitor Waste	PVC Waste	
	5000 metric ton/yr	335 metric tons/yr	6700 metric tons/yr
Estimated Capital Investment, millions of dollars	3.65	1.30	7.80
Estimated Operating Costs, dollars per metric ton			
Operating Labor	79.20	380.30	44.50
Auxiliary Fuel	307.00	185.60	185.60
Utilities, Chemicals, and Freight	92.10	28.90	28.90
Maintenance	65.70	124.50	37.30
Capital Related Items	197.10	1,047.70	285.70
Total Estimated Operating Cost, dollars per metric ton	741.00	1,767.00	582.00

Examination of the capital investments for pyrolysis of rubber wastes and the rotary kiln incineration of PVC wastes show the effects of large capacity facilities on the unit cost of thermal destruction. These changes in unit costs are principally related to labor and capital charges; moreover, the waste from a single process manufacturing facility will often be less than the annual capacity of a conventionally sized thermal destruction system.

The technical and economic uniqueness of the destruction of organic chlorides in cement kilns while simultaneously utilizing the released energy and assisting in controlling the quality of the cement is difficult to present in a manner which can be related to any of the other thermal destruction methods. If the organic chloride wastes are considered, economically, only for their energy content, then a clear economic advantage cannot be established other than, possibly, by comparison with other methods of thermal destruction. The many variables that would have to be considered in such a comparison would be so site specific as to make the calculated costs meaningless. On the other hand, for cement plants requiring control of alkali via chloride usage, a case of economic viability can be made when comparing the use of organic chlorides with other chloride sources. Thus the destruction of organic chlorides in a cement kiln may be a very attractive method when considered against other alternatives and will warrant serious technical and economic consideration when dealing with these difficult wastes.

4. DISCUSSION OF RESULTS

4.1 EFFECTIVENESS OF THERMAL DESTRUCTION METHODS

Thermal destruction of organic chemical wastes was shown to be highly effective, attaining destruction efficiencies of over 99.9 percent in four types of systems: liquid injection incinerator, fluidized bed incinerator, rotary kiln and cement kiln. In the case of wet oxidation, a lower (approximately 90 percent) destruction efficiency is expected because of process limitations. In the case of pyrolysis, thermal destruction was also found to be effective for two out of three wastes tested; these results cannot easily be expressed in terms of destruction efficiencies.

The effectiveness of thermal destruction found in these tests was undoubtedly partially attributable to the fact that the facilities tested generally represented the best practices of the state of the art. It is surmised that the effectiveness of a thermal destruction system, while dependent significantly upon conditions such as temperature, residence time, and turbulence, will be influenced by the attention given to controlling operation conditions. Such control is particularly significant in the operation of thermal destruction systems because the effects of any malfunctions usually become immediately apparent whereas malfunctions in other disposal methods, such as landfills, may result in long time delays before effects are evident. The capability of operating over a wide range of conditions, especially with respect to physical properties of wastes, is an important consideration in the selection of a method of thermal destruction, because the physical and chemical characteristics of a given chemical waste will vary over significant ranges. Consequently, the rotary kiln incinerator is most often chosen as a most versatile type; however, it is often coupled with a liquid-injection incinerator in order to provide the greatest degree of versatility. Other thermal destruction systems or combinations are less versatile and are selected because of unique capabilities and not wide range versatilities.

4.2 SELECTION OF FACILITIES FOR THERMAL DESTRUCTION OF CHEMICAL WASTES

The results of this program indicate that it is possible to select a type of thermal destruction for a waste if the physical and chemical properties are reasonably well-known. Of the fourteen wastes tested during this program, thirteen were found to have been effectively destroyed by the original thermal method chosen for this destruction as discussed below.

4.2.1 Liquid Injection Incineration of Hexachlorocyclopentadiene and Ethylene Manufacturing Wastes

The ethylene waste incineration proved relatively straightforward and trouble-free, and the waste was well matched with the design of the Marquardt liquid injection incinerator. However, the ethylene waste possesses physical and chemical properties of a distillate oil, and appears to be a good candidate for direct use as boiler fuel or as a supplemental fuel in the destruction of other industrial wastes. Conversely, hexachlorocyclopentadiene waste was a dark brown, dense and viscous liquid with suspended, wax-like particulate matter. It had a low heating value and would not sustain combustion without auxiliary fuel. In this test program, the hexachlorocyclopentadiene waste was destroyed effectively when blended with No. 2 fuel oil to facilitate the injection process and to provide heat for the combustion process. A better alternative would be to blend the chlorinated waste with the ethylene manufacturing waste, leading to the simultaneous destruction of these two wastes in the liquid injection incinerator without the added cost of auxiliary fuel.

4.2.2 Pyrolysis of API Separator Bottoms, Styrene Production Waste and Rubber Manufacturing Waste

These wastes were selected for pyrolysis, based on information obtained from the waste generators. Of the wastes actually received for testing, only the rubber waste conformed to these expectations and was truly representative of the type of waste for which pyrolysis might be expected to be a leading method of treatment. For the API waste, pyrolysis is technically feasible but probably not economically attractive compared with the alternative of combustion in a fluidized bed incinerator. For the styrene waste, pyrolysis has no advantages but has some disadvantages. Considerable quantities of carbon particulates were generated in the pyrolysis of the styrene waste and deposited in the off-gas duct work, thus representing both a loss of fuel value and a potential handling problem. The styrene waste, with its low viscosity, high heating value, and high sulfur content, can best be blended with a low sulfur fuel oil or liquid waste (such as the ethylene manufacturing waste) and used as boiler fuel. The rubber manufacturing waste, with about 80 to 90 percent of the organic material in the waste converted to vapor form suitable for energy recovery, was an ideal candidate for pyrolysis. The waste was also in a physical form (semi-solid lumps) which would make it very difficult to destroy in most types of thermal equipment, except a rotary kiln.

4.2.3 Fluidized Bed Incineration of Methyl Methacrylate Monomer Waste and a Phenolic Waste

The methyl methacrylate waste is a flammable liquid. Its vapor is heavier than air and may travel a considerable distance to a source of ignition and flash back. Also, at elevated temperatures, such as in fire conditions, polymerization may take place. For these reasons, the fluidized bed incinerator, with its nearly isothermal conditions and lower operating temperature, is ideal for the destruction of the methyl methacrylate waste. The aqueous phenol waste was matched to the fluidized bed incinerator because of 1) its ability to handle suspended solids, and 2) its lower operating temperature resulting in lower thermal energy requirement for converting the water contained in the waste to steam at the incineration temperature. Incineration of each waste was accomplished with high destruction efficiencies in the fluidized bed reactor, and no bed defluidization problems were encountered. An alternative method for the disposal of these two aqueous wastes would be wet air oxidation.

4.2.4 Wet Air Oxidation of Coke Plant Waste and Amiben® Manufacturing Waste

Both of these wastes were selected because they were aqueous solutions containing oxidizable pollutants and because they had low heating values.

In addition, the Amiben® waste, with its high sodium salt content, would cause severe defluidization problems in a fluid bed reator. The results of the tests indicated that wet air oxidation was suitable for the destruction of both the coke plant waste and the Amiben® waste, although further treatment of the aqueous effluent stream would be required before discharge to the environment.

4.2.5 Rotary Kiln Incineration of Vinyl Chloride Monomer Waste

The waste selected for testing was a stream containing vinyl chloride monomer, generated in the production of polyvinyl chloride (PVC). The waste was matched with a rotary kiln because this type of incinerator can readily handle wastes with high solids content. The test results showed that the PVC waste can be effectively destroyed in a rotary kiln without detectable emissions of vinyl chloride monomer.

4.2.6 Rotary Kiln Incineration of Capacitors Containing PCB, and Liquid Injection Incineration of Nitrochlorobenzene

The two wastes tested, PCB-containing capacitors and nitrochlorobenzene production waste, were selected on the basis of their suitability for destruction in a rotary kiln incinerator. Nitrochlorobenzene waste was to be burned in the kiln, but did not atomize properly in the kiln burner nozzle. After being mixed with No. 2 oil, the nitrochlorobenzene was fed through the liquid injection burner which fired the afterburner. Incineration of each waste was accomplished with high effectiveness, thus indicating the suitability of rotary kiln for PCB capacitor waste (especially in hammermilled form) destruction and the suitability of liquid injection incinerator for nitrochlorobenzene waste destruction.

4.2.7 Cement Kiln Incineration of Chlorinated Hydrocarbons

Chlorinated hydrocarbon wastes, including polychlorinated biphenyls (PCBs), were burned in a wet process cement kiln. The experiment was conducted to determine whether chlorinated hydrocarbon wastes may be burned in a rotary cement kiln without causing adverse air pollution, and at the same time provide useful energy and a source of chlorides to reduce the alkalies in cement and improve its quality. The types of wastes included a blended chlorinated aliphatic, aromatic and alicyclic waste, and a blended chlorinated hydrocarbon waste with the aforementioned components plus chlorinated biphenyls. The test effort was conducted by Environment Canada with the participation of the U.S. Environmental Protection Agency through supplemental analytical studies by TRW. The test results indicated that all three chlorinated hydrocarbon wastes can be effectively destroyed in the wet process cement kiln, and had the additional beneficial effect of improving the quality of cement. From the point of view of resource recovery, the match between industrial chlorinated hydrocarbon wastes and wet process cement kiln is probably the most ideal combination among all the waste/incinerator design matches investigated in this program.

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4.3 ECONOMICS OF THERMAL DESTRUCTION

The diversity of thermal destruction facilities and the wide variations in chemical and physical properties of the wastes investigated make it extremely difficult to compare the estimated costs in a meaningful manner. However, a number of general observations are useful. First, the estimated costs for thermal destruction in both capital and operating charges are certainly much greater than those which are presently incurred by land disposal; furthermore, it is expected that the future costs for disposal into controlled landfills, if permitted, would be lower than for thermal destruction. Secondly, thermal destruction will be utilized principally for those chemical wastes which contain hazardous components for which other methods of treatment or disposal are restricted either by regulations or special environmental considerations.

Experience indicates that wastes which contain only carbon, hydrogen, and oxygen and which can be handled in power generation systems can be destroyed in a way that reclaims some of their energy content. These types of wastes may also be utilized for judicious blending with wastes having low energy content, such as the highly chlorinated organics, in order to minimize the use of purchased fossil fuel and thereby limit the use of a valuable resource. On the other hand, rising energy costs will not be a significant deterrent to the utilization of thermal destruction methods where they are clearly indicated to be the most desirable method on an environmental basis.

In this test program, the cost of energy, especially as auxiliary fuel, was correlated with other variable costs, principally chemicals for controlling air pollution. This is because the wastes with low energy content were also those that contain large amounts of elements other than carbon and hydrogen (e.g., chlorine as in the hexachlorocyclopentadiene and PCB capacitor wastes) or both chlorine and water as in the PVC waste. Reductions in operating cost achievable by substitution of appropriate waste streams for purchased fuel are not as large as might have been anticipated.

In general, the largest single contribution to the operating cost for thermal destruction of chemical wastes was found to be capital related charges. When based on the premise that a thermal destruction facility is treated as an economic entity, these amounted to 1/3 to 1/2 of the total cost in most cases.

Because of the significant reductions in unit cost of thermal destruction achieved by large capacity facilities, and because the waste from a single process manufacturing facility will often be less than the annual capacity of a conveniently sized thermal destruction system, it seems likely that the historical trend in thermal destruction facilities will continue. That is, the thermal destruction facilities will be operated either as a toll operation by a private firm or, if captively owned by a manufacturing company, will serve a manufacturing complex or group of plants in a geographical zone of limited extent.

Thermal destruction methods are technically viable and environmentally desirable, although the high unit costs will cause industry to prefer to utilize other less costly alternatives if they are acceptable to regulatory agencies.

5. DETAILED SUMMARIES OF FACILITY TESTS

Highlights of the individual facility tests are briefly summarized in the previous sections. In this section, each facility test will be described in more detail. Descriptions include:

- Facility process design,
- Analysis of wastes tested,
- Sampling and analysis methods,
- Test procedures and conditions,
- Test results and interpretations, and
- Cost data.

Complete reports on each facility were published during the course of the program and are available from National Technical Information Service (References 3 through 9).

5.1 MARQUARDT - LIQUID INJECTION INCINERATION OF ETHYLENE AND HEXACHLOROCYCLOPENTADIENE WASTES

The Marquardt Company (TMC) incinerator, based on TMC's SUE® (for Sudden Expansion) burner, was selected for use on this program for several reasons. It utilizes a unique liquid injection configuration which has good air/fuel mixing properties. Development and application of the TMC incinerator system have been ongoing for over twelve years. It is commercially available and currently in use at various industrial facilities. This incinerator concept has been found to be effective in destroying waste propellants and solvents as well as chlorinated hydrocarbons such as herbicides and pesticides.

The two materials tested at TMC were ethylene waste and hexachlorocyclopentadiene (C-5,6) waste. A major selection criterion was physical compatibility with the incinerator, which required a liquid waste with very low suspended particulate levels. The ethylene waste was burned at three different combustion temperatures ranging from 1350° to 1750°C to evaluate the impact on destruction efficiency. To evaluate destruction of C-5,6 under different operating conditions, this waste was burned using three blends of fuel oil and waste in varying ratios from 2:1 to 1:1.

Sampling and analysis for the Marquardt tests were performed by TRW.

5.1.1 Process Description

Marquardt's liquid injection incinerator consisted of a SUE® burner (air, waste, and auxiliary fuel feed systems) and a high energy venturi scrubber. This facility is shown schematically in Figure 5-1. The basic system components are described in the following subsections.

The TMC incinerator was a well-instrumented test unit but similar in operation to their commercial configuration. The incinerator is scaled up to process larger waste throughputs by simply adding more basic units with proper manifolding, controls and an appropriately sized scrubber.

5.1.1.1 Incinerator and Reaction Tailpipe

The configuration of the SUE® incinerator and radiation cooled reaction tailpipe is shown in Figure 5-1. The burner consists of an inlet pipe connected to a large diameter combustion chamber by means of a flat plate. Fuel nozzles protruding through the plate spray the fuel radially into the inlet oxidizer stream. Burning occurs in the recirculation zone formed by the flat plate and the combustion chamber wall.

The combustion chamber wall is constructed of 310 stainless steel and is actively cooled by process air. The reaction tailpipe, also of 310 stainless steel, is cooled by radiation to the environment and provides a hot, walled chamber for completion of the incineration process. This unit operates at residence times of approximately 0.12 to 0.2 seconds. The

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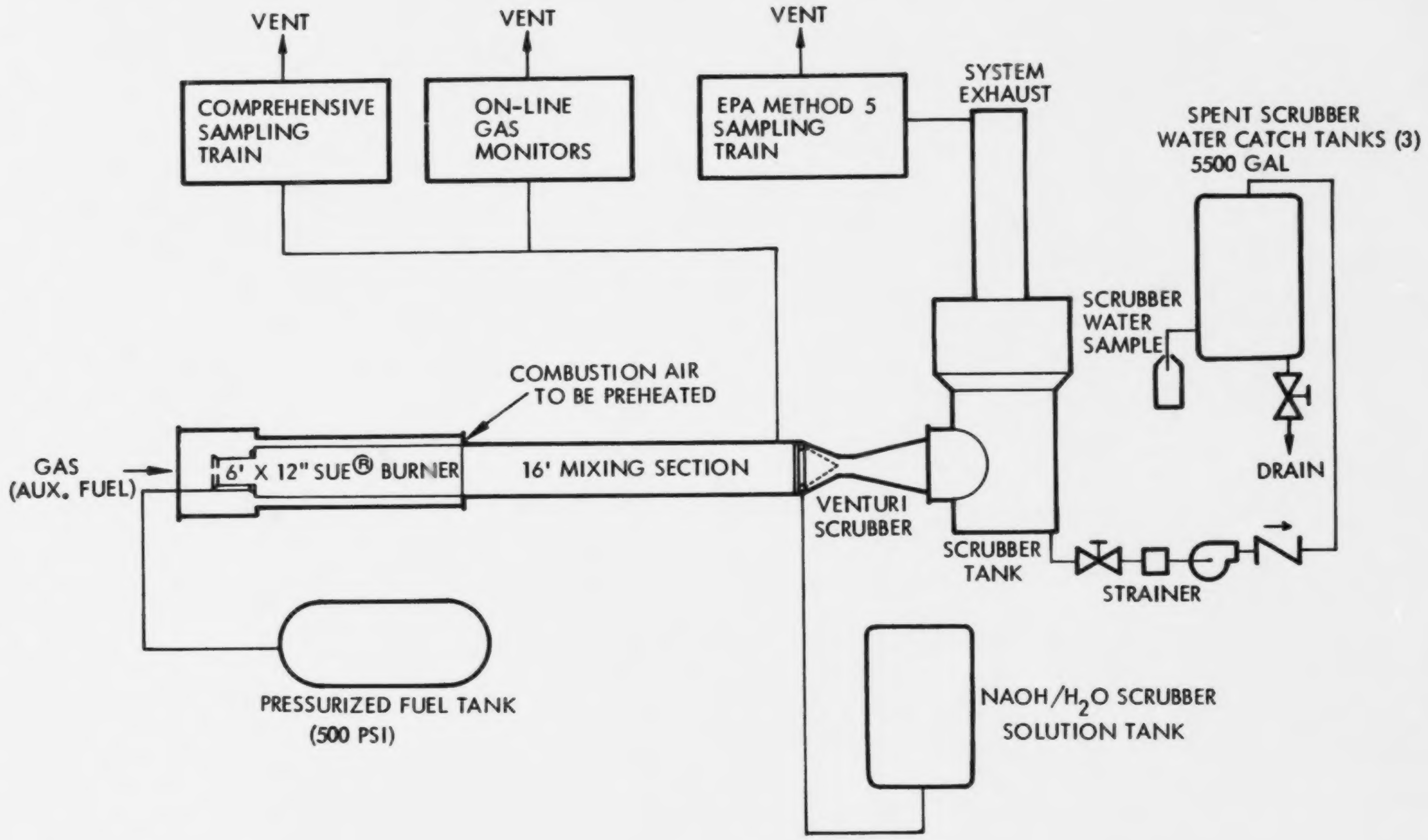
VENT
VENT
VENT
COMPREHENSIVE SAMPLING TRAIN
ON-LINE GAS MONITORS
EPA METHOD 5 SAMPLING TRAIN
SYSTEM EXHAUST
SPENT SCRUBBER WATER CATCH TANKS (3) 5500 GAL
SCRUBBER WATER SAMPLE
COMBUSTION AIR TO BE PREHEATED
GAS (AUX. FUEL)
6' X 12" SUE® BURNER
16' MIXING SECTION
VENTURI SCRUBBER
SCRUBBER TANK
DRAIN
STRAINER
PRESSURIZED FUEL TANK (500 PSI)
NAOH/H2O SCRUBBER SOLUTION TANK

Figure 5-1. TMC Test Facility

incinerator was designed for a continuous feed rate of 190 to 230 liters per hour and a maximum wall temperature of 1650°C.

5.1.1.2 Air and Fuel Feed Systems

Combustion air at the test site was supplied from the 4,140-kilopascal (600 psi) facility storage tanks. However, commercial installations utilize conventional forced draft fans for combustion air. Waste fuel was fed to the incinerator from a pressurized tank, through a 5-micron filter, a remote control valve, and a turbine flowmeter. The fuel line was purged with N_2 after use. A recirculation system was used to mix the tank contents. In commercial practice, the waste feed would be pumped from a run tank into the incinerator. Propane gas was used to preheat the incinerator system to approximately 815°C before introduction of the waste liquid; once combustion was established with the waste fuel, the propane was turned off. The No. 2 diesel oil that was used to support combustion of the C-5,6 waste was blended with the waste directly in the feed tank and fed to the liquid injection burner.

5.1.1.3 Instrumentation

Instrumentation capability provided by the Marquardt facility for this test program included measurements of all process parameters, including pressures, temperatures, and mass flow rates. In addition, on-line gas analysis of combustion products (CO, NO and CH_x) was conducted.

5.1.1.4 Emission Controls

Atmospheric emissions from the combustion of liquid wastes during the Marquardt incineration tests were controlled by a high energy venturi scrubber system. The major components of the scrubber system are:

- Venturi Scrubber and Separator Tank

  Quenching and scrubbing water with caustic solution was injected at the venturi inlet and mixed with the combustion gas at velocities up to 125 m/sec in the venturi throat. The separator tank is equipped with a metex screen demistor.

- Caustic Solution and Water Supply System

  When burning the C-5,6 waste, caustic solution was also injected to neutralize the HCl and Cl_2 in the combustion products. Caustic (approximately 10 to 12 percent NaOH in water) was injected at a rate about three times that required to neutralize the theoretically expected amounts of HCl.

- Scrubber Liquid Collection System

  Spent scrubber water was collected in catch tanks. The collected liquid was discharged to the facility's reservoir, analyzed and neutralized, as required, before release to the municipal sewer system.

5.1.2 Test Description

5.1.2.1 Wastes Tested

Ethylene Manufacturing Waste

The ethylene manufacturing waste is a relatively nonhazardous, high heating value waste. It is generated at a rate of approximately 15 million kilograms per year.

The waste obtained was a clear, light brown solution with no apparent sediment or particulate at room temperature. It had a specific gravity of about 0.9 and a heating value of slightly more than 10,000 kcal/kg (18,000 Btu/lb). Its chemical composition was approximately 89 percent carbon and 9 percent hydrogen. Halogens (as chlorine) were about 0.004 percent. Sulfur and nitrogen contents were 1.3 and 0.13 percent, respectively. A viscosity of 1.28 centistokes (at 22°C) allowed this material to be transferred and injected into the incinerator without preheating or other conditioning. Organic components of the waste, summarized in Table 5-1, were primarily unsaturated cyclic and aromatic compounds. No organic sulfur compound could be identified. Thus, the 1.3 percent sulfur found by elemental analysis was most likely present in an inorganic form. Total inorganic (ash) content of the ethylene waste was less than 0.01 percent. Trace elemental analysis showed no metals present at greater than 1 ppm levels.

TABLE 5-1. COMPOSITION OF ETHYLENE MANUFACTURING WASTE SAMPLE

Compound	Approximate Concentration (percent)
Cyclopentadiene	< 0.1
1, 3, 5-Hexatriene	< 0.1
Methylcyclopentadiene	< 0.1
Benzene	30.
Cyclohexadiene	20.
Toluene	20.
Xylene	3.
Styrene	20.
Methyl Styrene	0.8
Indene	5.0
Methylindene and Divinyl Benzene	1.
Naphthalene	3.
Ethyl Naphthalene	0.2

Hexachlorocyclopentadiene Manufacturing Waste

This highly chlorinated waste is produced at a rate of 4.5 million kilograms annually. It would not sustain combustion without auxiliary fuel; its heating value was only 2,400 kcal/kg (4300 Btu/lb). The C-5,6 waste was a dark brown liquid with suspended, waxlike particulate matter. Specific gravity was in excess of 1.7, while its viscosity was 11.3 centistokes (at 22°C). The waste was miscible in No. 2 fuel oil which facilitated injection and combustion in the liquid incinerator. The chemical composition of a sample of the C-5,6 waste was approximately 21 percent carbon, 0.67 percent hydrogen, 0.37 percent nitrogen, 0.016 percent sulfur, and 77 percent total halogens (as chlorine). Hexachlorocyclopentadiene (C_5Cl_6) and octachlorocyclopentene (C_5Cl_8) were the major organic waste components found in two separate samples of the C-5,6 waste, as shown in Table 5-2.

Total inorganic (ash) content of a sample of the waste was ~0.04 percent. Elemental inorganics found were primarily innocuous metals, such as Fe, Si, Al, Na, and Ca. Lower and trace ppb levels were found for numerous elements.

5.1.2.2 Sampling Methods

Procedures used were those specified in Section 3.3, with the following modifications:

- A Teflon valve was added to the glass connector between the sorbent trap and the first impinger through which glass bulbs were filled with the sample gas to be analyzed for any volatile or gaseous components not collected by the sorbent trap.
- For the C-5,6 test burns where large quantities of HCl were produced by combustion, a large, two-liter impinger was added between the solid sorbent trap and the first modified Greenburg-Smith (G-S) impinger. This large impinger was then charged with caustic solution.

TABLE 5-2. COMPOSITION OF C-5,6 WASTE

Compound	Approximate Concentration (percent)
C_5Cl_6 Hexachlorocyclopentadiene	50-65
C_5HCl_7 Heptachlorocyclopentene	3-5
C_5Cl_8 Octachlorocyclopentene	30-45
Other Minor Constituents	1-2

All of the spent scrubber water samples were obtained from a tap downstream of the tank which holds the water after it has passed through the venturi scrubber. The city water control sample was taken from a line which supplies water to the venturi scrubber. Samples of solid residue (or clinker) which accumulated in the combustor were collected when the burner assembly was removed after each test burn.

5.1.2.3 Analysis Methods

Methods used were those specified in Section 3.3.

5.1.2.4 Test Procedures

Tests at TMC were run following the basic procedures described in Section 3.2. The test series for each waste consisted of three test burns. For the ethylene waste three different combustion temperatures were targeted to be achieved by varying the fuel feed rate and the air:fuel ratio. For the C-5,6 waste the temperatures were to be kept at optimum burn conditions while reducing the auxiliary fuel:waste ratio.

TMC standard safety procedures for handling and incinerating industrial chemicals were observed during this test program. The residual ethylene and C-5,6 waste materials along with the empty drums left from the test burns were disposed of by a contract disposal firm in accordance with all applicable regulations.

5.1.3 Test Results

A summary of the test results is presented in Table 5-3, beginning with the range of test conditions for each waste, including combustion temperature, residence time, and waste feed rate. The summary presented in this table also covers analytical results from samples taken during testing, destruction efficiency calculations based on those results, and costs for commercial scale application of TMC's incineration system. These areas are discussed further in the following sections.

5.1.3.1 Incinerator Operating Conditions

For the three test burns of ethylene waste, the fuel feed rate was varied from 1.4 to 2.0 kg/min. at fuel/air ratios of 0.040 to 0.057. Combustion temperatures were 1150° to 1450°C with residence times of 0.14 to 0.19 seconds. The C-5,6 waste was blended with No. 2 oil at ratios of 1:2, 1:1.5, and 1:1, and these blends were then fed at rates of 2.0, 2.4, and 3.0 kg/min., respectively. Fuel/air ratios ranged from 0.060 to 0.086 with combustion temperatures of 1230° to 1260°C and residence times of 0.17 to 0.18 seconds.

5.1.3.2 Characterization of the Incineration Process

The composition of the combustion chamber effluent, in terms of inorganic gases and total volatile hydrocarbons (as methane), is shown in Table 5-4.

TABLE 5-3. MARQUARDT RESULTS SUMMARY

	Ethylene Waste	C-5,6 Waste
Combustion Temperature (°C)	1349-1752	1348-1378
Residence Time (sec)	0.14-0.19	0.17-0.18
Feed Rate (kg/min)	1.4-2.0	2.0-2.9(1)
Quality of Stack Emissions:		
Particulate (mg/m^3)	20-25	36-113(2)
Trace Metals (mg/m^3)	0.001-0.003 Pb	0.003-0.006 Pb 0.034-0.065 Mn
Quality of Combustion Gas:		
Total Organics (mg/m^3)	13-22	21-27
Waste Content (mg/m^3)	Not Detected (<0.02)	Not Detected (<0.02)
Trace Metals (mg/m^3)	0.002-0.003 Pb	0.55-1.40 Pb 0.077-0.19 Mn 0.090-0.33 Co
Quality of Scrubber Water:		
Total Organics (mg/liter)	Not Significant(3)	Not Significant(3)
Trace Metals (mg/liter)	0.02 Pb	0.21-0.54 Pb
Quality of Solid Residue (clinker):		
Waste Content (mg/g)	1.8-2.4	Not Detected (<.026)
Destruction Efficiency:		
Total Organics (percent)	99.95-99.96	99.94-99.95
Waste Constituents (percent)	>99.999	>99.999

(1) Mixture of C-5,6 and No. 2 oil; feed rate of C-5,6 alone is 0.66-1.5 kg/min.

(2) 85-90 percent of stack particulate content was calculated (based upon sodium analysis) to be NaCl produced by the reaction of the caustic scrubber solution with HCl and CO_2.

(3) Levels not significantly higher than background water samples.

TABLE 5-4. TOTAL GAS COMPOSITION IN THE COMBUSTION ZONE BY VOLUME

Run No. and Fuel Description	O_2 ( )	CO_2 ( )	N_2 (%)	H_2O (%)	HCl ( )	Cl_2 (ppm)	CO (ppm)	NO_x (ppm)	HC (ppm)	SO_2 (ppm)
Fuel Oil Background										
I	6.3	9.8	73.0	10.9	-	-	12	170	10	15-20
Ethylene Waste										
II	7.2	10.3	74.0	8.5	-	-	17	200	5-10	100-200
III	9.4	9.3	73.4	7.9	-	-	17	150	5-15	100-200
IV	4.9	11.5	74.2	9.4	-	-	22	520	5	100-200
C-5,6 Fuel Oil										
V	8.1	8.4	69.6	12.7	1.15	< 0.05	20	145	10-25	5
VI	5.6	9.7	68.8	14.2	1.64	15	17	140	35-65	6
VII	5.5	9.5	67.9	14.7	2.35	56	17	120	30-35	5

Analysis of the samples collected by the hot zone sampling train did not reveal the presence of any waste constituents or other hazardous organic compounds at an estimated detection limit of 0.1 mg/m^3. Other compounds identified in these samples, at levels of 0.1 to 4 mg/m^3, were found to be silicones and oxygenated organics, believed to be contaminants. The amount of total organic materials found by all analysis techniques ranged from 10 to 25 mg/m^3. However, the materials found were only silicones, alkyl hydrocarbons, and alkyl esters of phthalic acid. Concentrations of all metals in the filter and impinger samples of the hot zone train were very low for the ethylene waste burns with only zinc, at 0.01 mg/m^3, showing any increase above the background No. 2 oil burn. Generally, higher levels were found for the C-5,6 waste burns; 0.56 to 1.4 mg/m^3 of lead, 0.09 to 0.34 mg/m^3 of cobalt, 0.03 to 0.14 mg/m^3 of chromium, and 0.10 to 0.29 mg/m^3 of manganese were found in the combustion gas.

Standard EPA Method 5 test results showed particulate loadings of 20 to 25 mg/m^3 for the No. 2 oil and ethylene waste tests. Particulate loadings of 36 to 114 mg/m^3 were obtained for the C-5,6 tests, but 85 to 90 percent of the particulate matter from these tests was found to be sodium salts generated by the reaction of the caustic scrubber with HCl and CO$_2$. For the background and ethylene waste burns, no hazardous metals were found to be present in the stack gas above 0.1 mg/m^3 for any of the waste tests. For the C-5,6 waste burns the significant metals found were 0.01 to 0.06 mg/m^3 of lead, 0.003 to 0.01 mg/m^3 of cobalt, 0.008 to 0.04 mg/m^3 of chromium and 0.03 to 0.17 mg/m^3 of manganese. For the ethylene test, the stack gas was found to contain SO$_x$ at levels consistent with the 1.3 percent sulfur in the waste feed.

Samples of scrubber water were analyzed for both organic and inorganic content. No indication of any waste or other hazardous constituents was detected at levels above 0.1 mg/liter. Trace metal concentrations in the scrubber water samples ranged from 0.1 to 0.5 mg/liter.

A burner head residue was found to form during incineration of both waste materials. These residues were typically 90 to 99 percent carbon. The residue collected from the ethylene tests contained on the average one percent extractable organics. Approximately 1/5 of these extractables were identified as uncombusted waste constituents. The residue extracts contained aliphatic and aromatic hydrocarbons, but no evidence of any polynuclear aromatic hydrocarbons larger than naphthalene. The residue from the C-5,6 tests contained only 0.3 percent extractable organics which were determined to be primarily aliphatic hydrocarbons. There was no evidence of any chlorinated compounds in these extracts. Other than Fe, Si, Na, and Mg, no metals were detected in any of the burner head residue samples at levels above 500 ppm.

5.1.4 Interpretation of Results

The waste destruction performance is summarized in Table 5-3 for both total organics and the specific waste constituents. Since no waste constituents were found in the combustion gas samples, the waste destruction efficiency is quite high (>99.999%). Destruction efficiencies for total organics were essentially the same for all tests and averaged 99.95 percent. The total organic efficiencies were calculated by adding the on-line hydrocarbon analyzer measurements to the amount of total organics found in the combustion zone sampling train samples.

Chemical composition, combustion characteristics, and emissions of the ethylene waste are so nearly identical to No. 2 oil that the use of this waste as a primary or secondary boiler fuel should be seriously considered. With the possible exception of the formation of clinker, which appears to have small impact, the incineration of this type of ethylene waste is clean and efficient.

The results of these tests indicate that the C-5,6 waste can be effectively destructed in a liquid injection incinerator. No evidence of C-5,6 or any other chlorinated organic was found in any of the samples, including the coke-like burner head residue referred to as clinker. However, because of the tarry residual in the waste, the C-5,6 may be better matched to rotary kiln incineration, which can accommodate tars and sludges.

To determine the acceptability of the trace metal concentrations measured in the scrubber waters, the Los Angeles County Sanitation District Phase I concentration limits for point source discharge to a sewer were consulted. The heavy metal concentrations were all at least a factor of ten below the most stringent maximum allowable concentration for these listed metals which is 10 mg/liter (ppm). It was concluded that these scrubber wastes were sewered in accordance with local regulations.

5.1.5 Incineration Costs

Individual economic analyses were performed to determine the costs of incinerating, on an industrial basis, the annual source plant productions of the two waste materials tested at The Marquardt Company (TMC). The basis for the preparation of cost estimates is presented in Section 3.6.

The capital investment for the facility to incinerate 15 million kilograms per year of ethylene manufacturing wastes, shown in Table 5-5, is based upon a design concept which employs two SUE burner-incinerator-scrubber systems in parallel, fed by a common automatic feed system. The facility costs include, as common use items, an ethylene manufacturing waste storage tank, a scrubbing water supply system, and a settling pond. It was assumed that the only fuel needed for the incinerators was the ethylene manufacturing wastes. The size of the facility was based on a ninety percent plant operating factor and 15 million kilograms per year of ethylene wastes.

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The capital investment for the plant required to incinerate 4.5 million kilograms per year of the hexachlorocyclopentadiene waste mixture, also shown in Table 5-5, is based on sizing the incinerator conservatively on the heat of combustion resulting from feeding a 1:2 weight ratio of C_5Cl_6 waste and No. 2 fuel oil. The plant design concept includes one SUE burner incinerator-scrubber system, an automated feed system, a waste storage tank, a No. 2 fuel oil storage tank, and the caustic soda solution storage tank. Auxiliary equipment also includes the scrubbing water supply system tank and pump, the scrubber wastes collection/settling pond, and a pH control system.

TABLE 5-5. CAPITAL INVESTMENT AND OPERATING COSTS FOR LIQUID INJECTION INCINERATION OF ETHYLENE WASTE AND HEXACHLOROCYCLOPENTADIENE WASTE

	Ethylene 15,000 Metric tons/yr	Hexachlorocyclopentadiene 4500 metric tons/yr
Estimated Capital Investment $ millions	1.82	1.63
Operating Costs, $/metric ton		
Operating Labor	20.60	69.50
Auxiliary Fuel	-	94.00
Utilities, Chemicals, Freight	5.90	201.30
Maintenance	9.70	30.00
Capital Related Items	32.50	97.20
Total Estimated Operating Cost	69.00	492.00

5.2 SURFACE COMBUSTION - PYROLYSIS OF API SEPARATOR BOTTOMS, STYRENE, AND RUBBER WASTES

Pyrolysis was selected as a method for testing in this program because it offers the potential for recovery of resources from waste materials. A full-scale pyrolysis facility within the continental United States which would be available for this test program could not be located. Because of the high priority assigned to the resource recovery potential of pyrolysis, it was decided to conduct a series of tests using the pilot plant pyrolysis unit operated by the Surface Combustion Division of Midland-Ross Corporation in Toledo, Ohio. The wastes tested at this facility were:

- Petroleum refinery waste (Centrifuged API Separator bottoms)
- Styrene production waste
- Rubber manufacturing waste

5.2.1 Process Description

In a pyrolysis process, material is thermally decomposed in a non-oxidizing environment. The usual objective is to convert a relatively high molecular weight hydrocarbon (or mixture) to a more convenient fuel form, especially one which burns more cleanly. In contrast to conventional incineration, which is intended to achieve complete oxidation, pyrolysis is intended to produce a product stream which contains a high energy content by virtue of its hydrocarbon concentration. This feature of the pyrolysis process is increasingly appealing with the advent of energy and raw material shortages. In addition, pyrolysis can be applied to tarry, semisolid, and solid organic chemical wastes that are not amenable to other treatment techniques.

The Surface Combustion pyrolysis/incineration system as used for this test program is shown schematically in Figure 5-2. This facility is a rotary hearth pyrolyzer which is coupled to a rich fume incinerator for combustion of the gaseous pyrolyzer effluent.

The pyrolyzer itself is the central piece of equipment in this system, but because of the physical nature of many of the chemical wastes treated by pyrolysis (e.g., semisolid rubber waste), the feed system required also becomes a very important operating consideration. The liquid wastes, API separator bottoms and styrene tar, were fed by pumping at room temperature. The rubber waste was fed by a specially designed mechanism. A pneumatic cylinder was used to operate a piston to push the waste through an orifice and then through a spreader nozzle.

The rotary hearth is 76 cm (2.5 ft) in diameter and 2.5 cm (1 inch) deep. The hearth speed can be varied from 1/2 to 3 revolutions per hour. The pyrolyzer is equipped with a 63,000 kcal/hr (250,000 Btu/hr) burner.

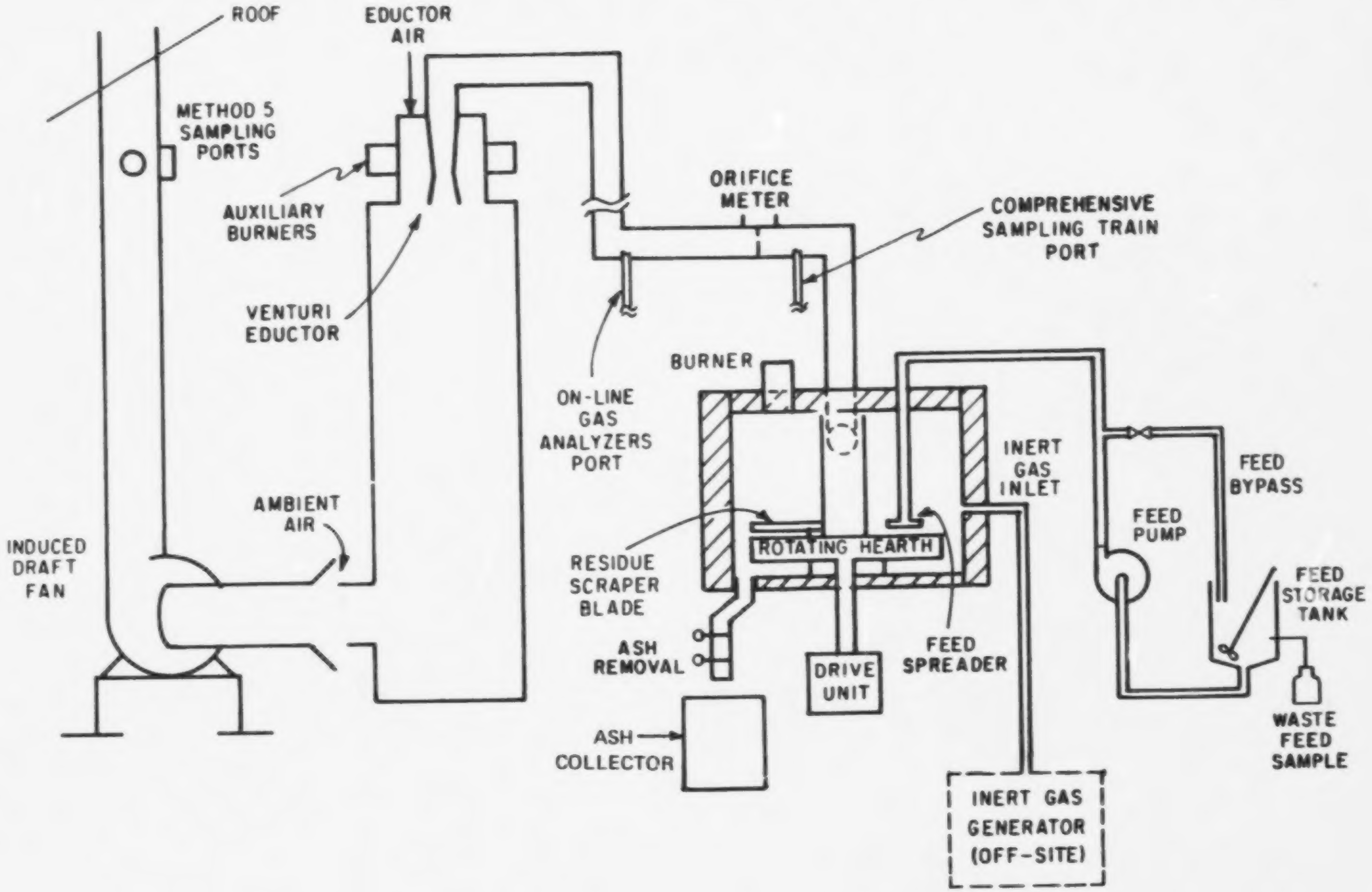

ROOF
EDUCTOR AIR
METHOD 5 SAMPLING PORTS
AUXILIARY BURNERS
VENTURI EDUCTOR
ORIFICE METER
COMPREHENSIVE SAMPLING TRAIN PORT
BURNER
ON-LINE GAS ANALYZERS PORT
INERT GAS INLET
FEED BYPASS
FEED PUMP
AMBIENT AIR
INDUCED DRAFT FAN
RESIDUE SCRAPER BLADE
ROTATING HEARTH
FEED STORAGE TANK
ASH REMOVAL
DRIVE UNIT
FEED SPREADER
WASTE FEED SAMPLE
ASH COLLECTOR
INERT GAS GENERATOR (OFF-SITE)

Figure 5-2. Schematic of Test Pyrolyzer/Incineration System

A plow mechanism is used to remove residue from the hearth. Temperature and pressure in the pyrolyzer are automatically controlled. The feed zone of the pyrolyzer was continuously purged with an inert gas during the operation to improve visibility and cool the feed zone as well as control the oxygen concentration. Pyrolyzer pressure was maintained slightly above atmospheric.

The rich fume incinerator is equipped with two throat mix burners of 126,000 kcal/hr (500,000 Btu/hr) capacity each. Auxiliary fuel was also used in the incinerator in this test series. The incinerator is equipped with temperature controller and high limit safety shut-off instrumentation. The burners are mounted at the top and gases flow downward and are exhausted by an induced draft fan after dilution with ambient air. The fan capacity is about 113 std. m^3/min (4,000 scfm).

5.2.2 Test Description

5.2.2.1 Wastes Tested

The chemical wastes selected for testing at this pyrolysis facility were three which, based on descriptions originally provided by the waste generators, would be good candidates for resource recovery and/or would be difficult to treat in other types of thermal destruction facilities. The materials actually received for testing differed substantially from expectations, illustrating the wide variability in composition of wastes from chemical production processes.

API Waste

The API waste actually tested was a grey-black, shiny gelatinous material which had a strong and somewhat irritating odor. The waste was about 70% by weight water and about 13% by weight organic material. Elemental analysis of the organic portion showed the following composition: C, 84.72%; H, 11.87%; N, 0.16%; and S, 1.24%. The organic components of the representative waste feed were found to be 42.7% aliphatic hydrocarbons (primarily unsaturated), plus aromatic hydrocarbons of up to 3 fused rings, alkyl derivatives of these aromatics, and phenyl-substituted alkanes. Higher molecular weight polynuclear aromatic hydrocarbons were not identified in the waste.

Examination of a sample of waste by spark source mass spectrometry (SSMS) showed the presence of some 63 elements. A number of elements that were found at substantial concentrations (>100 ppm) are recognized as potentially hazardous. These include zinc (1000 ppm), chromium (420 ppm), fluorine (240 ppm) and lead (210 ppm).

The higher heating value of the waste was estimated at 1390 kcal/kg (2500 Btu/lb).

Styrene Waste

The styrene waste was a brown-black viscous liquid with some suspended particulate. It had a pungent odor. The waste was 98% by weight organic material. Elemental analysis showed the following composition: C, 84.46%; H, 6.96%; N, 0.02%; and S, 7.86%. A high sulfur content had not originally been expected for this waste; the waste generator confirmed that a process change had occurred and that elemental sulfur was now added during styrene production. The styrene waste was found to consist largely of unsubstituted (28%) and substituted (60%) aromatic hydrocarbon species of up to three fused rings. Higher molecular weight polynuclear aromatics were not identified in the waste. The sulfur was present primarily as the element.

Examination of a sample of waste by SSMS showed only low levels of materials generally recognized as hazardous. These included zinc (1.7 ppm), chromium (0.2 ppm) and lead (0.1 ppm).

The higher heating value of the waste was estimated to be 8.9×10^3 kcal/kg (16×10^3 Btu/lb).

Rubber Waste

The rubber waste was composed of slightly sticky, semisolid black lumps of various sizes. The waste was found to contain 33% by weight of organic material extractable with methylene chloride, 36% residue on extraction, and 30% water. Elemental analysis of the extractable organics showed the following composition: C, 79.53%; H, 10.10%; N, 0.08%; and S, 0.48%. Analysis of the extract by Gel Permeation Chromatography (GPC) showed that 34% of the material had molecular weight (MW) > 50,000; 27% had MW ≈ 1000 and 38% had MW ≈ 100. Low resolution mass spectroscopy indicated that approximately half of the lower molecular weight material was unsaturated aliphatic hydrocarbons. Overall, the data show that the rubber waste is a polymeric material composed of highly unsaturated and aromatic hydrocarbons. Higher molecular weight polynuclear aromatic hydrocarbons were not identified in the waste.

In all, 61 elements were detected in a waste sample by SSMS. Among the elements found at significant concentrations that are generally recognized as potentially hazardous were: chromium (130 ppm), lead (62 ppm), zinc (53 ppm), and fluorine (20 ppm). In a separate analysis, mercury was found at a level of 0.3 ppm.

The higher heating value of the waste was estimated to be 5500 kcal/kg (9800 Btu/lb).

5.2.2.2 Sampling Methods

The methods used for sample collection were those described for the overall test program (Section 3) with the following exceptions:

- The portion of the pyrolysis zone effluent fed to the on-line instruments was sampled with a 12.7 mm stainless steel probe and passed through an ice-cooled knock-out trap before entering the heat-traced line.

- The grab sample of pyrolyzer effluent was taken with a 12.7 mm quartz probe. A knock-out trap consisting of ice-cooled impingers was used upstream of the filter to collect readily condensable organics.
- The impingers downstream of the solid sorbent trap contained aqueous sodium hydroxide to collect acidic gases.
- The grab gas sample was taken from the bypass line of the hydrocarbon analyzer.

5.2.2.3 Analysis Methods

The methods used for analysis of the Surface Combustion samples were those described for the overall test program (Section 3.3). In addition, thermogravimetric analysis, boiling point distribution curves and gel permeation chromatography were utilized to reveal the distribution of boiling points and/or molecular weights of feed and effluent samples.

5.2.2.4 Test Procedures

Tests were run following the basic procedure described in Section 3.2. Pyrolyzer hearth residue samples were collected after system shutdown at the conclusion of each test.

5.2.3 Test Results

5.2.3.1 Pyrolyzer Operating Conditions

Table 5-6 summarizes the test conditions for three runs of each type of waste (API separator bottoms, styrene tar and rubber waste) and one background burn.

In the original test program, it was anticipated that several residence times and pyrolyzer temperatures would be tested for each feed. When the testing was actually conducted, however, it was necessary to use the maximum pyrolyzer temperature, 760°C (1400°F), and the maximum hearth speed (3 revolutions per hour) in most cases in order to adequately destroy the wastes. The maximum hearth speed was necessary in order to spread the wastes thinly enough on the hearth to allow their complete pyrolysis. With a pyrolyzer temperature of 760°C (1400°F) the temperature of the pyrolysis gas ranged from 590-650°C (1000-1200°F). The variable changed with each run was, therefore, the waste feed rate. The waste feed rate was varied to find the maximum feed rate consistent with an acceptable char or ash while operating at maximum temperature and minimum residence time.

5.2.3.2 Products of Pyrolysis

The products of pyrolysis are a vapor stream and a residual ash or char. The effectiveness of a pyrolysis process is generally assessed in terms of the vapor stream, since this is expected to contain the recoverable

TABLE 5-6. SUMMARY OF PYROLYSIS TEST CONDITIONS

Run No.	Waste	Waste Feed Rate		Inert Gas Flow		Pyro. Temp		Residence in Hot Zone	Incinerator Temperature	
		Kg/hr	(lbs/hr)	m3/hr	(SCFH)	(°C)	(°F)	(mins)	(°C)	(°F)
1	API Separator Bottoms	16.7	(36.7)	42.5	(1500)	760	1400	12.5	830	1520
2	API Separator Bottoms	14.7	(32.4)	42.5	(1500)	760	1400	12.5	830	1520
3	API Separator Bottoms	25.3	(55.6)	42.5	(1500)	760	1400	12.5	830	1520
4	Styrene Tar	5.3	(11.7)	44.7	(1580)	760	1400	12.5	830	1520
5	Styrene Tar	7.4	(16.3)	42.5	(1500)	650	1200	12.5	830	1520
6	Styrene Tar	10.0	(22.0)	42.5	(1500)	760	1400	12.5	880	1610
7	Background - No Feed	-	-	42.5	(1500)	760	1400	12.5	825	1515
8	Rubber Waste	12.2	(26.8)	42.5	(1500)	760	1400	15	825	1515
9	Rubber Waste	9.4	(20.7)	35.4	(1250)	760	1400	15	820	1510
10	Rubber Waste	7.3	(16.0)	34.7	(1225)	760	1400	15	820	1510

resource(s) (energy content and/or organic chemicals of commercial value), while the ash or char is usually destined for disposal. For the three wastes tested at Surface Combustion, the vapor stream was found to contain a wide variety of organic compounds, ranging from gases, at normal temperature and pressure, such as methane and acetylene, to high boiling (500°C) liquids and tars. The heavier, condensable components of these streams are aromatic compounds, including appreciable concentrations of polynuclear aromatic hydrocarbons. The residual ash in all tests was found to contain mostly (>80%) inorganic material. The results are summarized in Table 5-7 and are discussed briefly below.

API Waste

A total of about 70%-75% of the organic material in the waste was converted to a form which was combustible in the rich fume incinerator. Because the original waste was largely aqueous, this corresponds to only 9% by weight of the total waste feed. The pyrolysis gas was about 70% volatiles ($\leq C_6$) and about 30% condensable aromatics at normal conditions. The sulfur content of the pyrolysis gas was 136 mg/m^3 as sulfur. The pyrolysis gas contained 3.2% of polynuclear aromatic hydrocarbons in the condensable fraction. This is equivalent to a pyrolysis emission rate of about 350 mg/m^3.

The API waste contains substantially higher levels of trace metals than typical high ash fuels such as coal. The major portions of these are found in the solid residue from the pyrolyzer. Less than 5% of the lead and zinc content of the waste is found in the pyrolyzer gas.

The ash, or solid residue, amounted to about 20% by weight of the total API waste feed, and was about 85% inorganic material.

Total particulate loading at the stack was 23-88 mg/cu m. Sulfur dioxide levels in the stack gas were 30-50 ppm. Lead and zinc were found in the stack gas at 0.05 mg/cu m.

Styrene Waste

A total of about 57% of the organic material in the waste was converted to a form which was combustible in the rich fume incinerator. The pyrolysis gas was about 27% volatiles ($\leq C_6$) and about 73% condensable aromatics at normal conditions. The sulfur content of the pyrolysis gas was 753 mg/m^3 as sulfur. This was primarily carbon disulfide, carbonyl sulfide and sulfur dioxide. The pyrolysis gas was found to contain 1.6% of polynuclear aromatic hydrocarbons, as pyrene in the condensable fraction. This is equivalent to an emission rate of 400 mg/m^3.

The styrene waste contained only low levels of metals recognized as hazardous. The analyses indicate that none of these were present in the pyrolysis gas.

The ash, or solid residue, amounted to about 0.5% by weight of the total waste feed, and was about 96% inorganic material.

TABLE 5-7. SUMMARY OF TEST RESULTS

	API Waste	Styrene Waste	Rubber Waste
Distribution of Products			
Organic Vapors (% of Total Feed)	9	57	27
Ash (% of Total Feed)	20	<2	20
Remainder	Water	Soot	Water & Soot
Percent of Organics in Feed which were Found in Vapor	70	60	80
Percent of Organics in Feed which were Found in Ash	30	<0.01	8
Ratio of Light ($\leq C_6$) to Heavy Organics in Pyrolyzer Effluents	2.3	0.4	2.3
On-Line Instrument Data			
Hydrocarbons, % as methane	1.2-1.3	2.4-2.5	2.5-3.1
Carbon monoxide, ppm	1450-2175	2090-2240	1950-2125
Carbon Dioxide, %	10.8-11.1	10.7-11.0	9.9-10.1
Oxygen, %	0.0	0.0	0.0
Nitrous Oxide (NO), ppm	95-100	65-80	65-75

Total particulate loading at the stack was 28-43 mg/cu m. Sulfur dioxide levels in the stack gas were 100-200 ppm. No trace metals were detected in the stack gas.

Rubber Waste

A total of about 80% to 90% of the organic material in the waste was converted to a form which was deliverable to the rich fume incinerator. This corresponds to about 27% by weight of the original waste feed. The pyrolysis gas was about 70% true volatiles ($\leq C_6$) and about 30% condensable aromatics. The sulfur content of the pyrolysis gas was 189 mg/m^3 as sulfur. The pyrolysis gas was found to contain 2.1% of polynuclear aromatic hydrocarbons in the condensable fraction. This is equivalent to an emission rate of 490 mg/m^3.

The rubber waste contained significant concentrations of several metals recognized as potentially hazardous. The analyses indicated that these species were not present in the pyrolysis gas, but were concentrated in the ash.

The ash, or solid residue, amounted to about 20% by weight of the total waste feed, and was about 80% inorganic material.

Total particulate loading at the stack was 9 to 14 mg/cu m. Sulfur dioxide levels in the stack gas were 25 ppm. No trace metals were detected in the stack gas.

5.2.4 Interpretation of Results

The effectiveness of a pyrolysis process can be assessed in terms of the gaseous pyrolyzer effluent, since this is expected to contain the recoverable resource(s) (energy content and/or organic chemicals of commercial value). For the three wastes tested at Surface Combustion, the average conversion of organic material in the waste feed to organic material in the gaseous pyrolyzer effluent was 70% for API waste, 60% for styrene waste, and 80% for rubber waste. In each case, the chemical composition of the effluent was similar to that of residual oils or the products obtained from coking of coal.

The results of these tests indicate that certain potential adverse environmental impacts must be evaluated in any large-scale recovery of the energy value of pyrolyzer effluents. Using the API and rubber wastes, for example, the occurrence of $>125\ mg/m^3$ of sulfur in the vapors could lead to problems in meeting emissions standards for sulfur oxides from combustion systems. Other potential problems are (1) the 350 to 500 mg/m^3 of polynuclear aromatic hydrocarbons, a class which includes some species recognized as carcinogens and (2) the occurrence of small but detectable amounts of heavy metals such as the lead and zinc found in the API wastes. While these factors will have to be considered carefully in the design of an appropriate heat recovery system, they are by no means insurmountable problems. These problems will be similar to those encountered in coke-making, gasification of coal, and the combustion of residual oils.

Consideration of engineering aspects of the tests led to the following conclusions:

API Waste

The high viscosity and ash content would make this waste unsuitable for a conventional liquid injection incinerator. This waste could be handled in a fluid bed incinerator, or as these tests have shown, in a pyrolyzer. It would probably be more economical to dispose of this waste in a fluid bed incinerator, however, especially in view of the high water content and low heat value.

Styrene Waste

Samples of this waste obtained before the test program indicated a relatively high viscosity. The waste actually obtained for the test was of much lower viscosity and could have been burned in a conventional liquid injection incinerator. Upon pyrolysis of the highly unsaturated chemical components, considerable quantities of carbon particulates were generated which deposited in the off-gas duct work. This carbon particulate represents both a loss of fuel value and a potential handling problem. Pyrolysis thus involves some major disadvantages, compared to conventional incineration, for this waste.

Rubber Waste

This waste is in a physical form (semisolid lumps) which would make it very difficult to incinerate in virtually any other type of thermal destruction equipment. Even the destruction of this waste by pyrolysis requires that the waste be fed to the pyrolyzer in a thin enough layer on the hearth to allow complete pyrolysis. This can be accomplished by extruding the waste (in the proper thickness) directly onto the hearth.

An important factor in the thermal destruction of this waste by pyrolysis is the 80% to 90% efficiency of conversion of the organic components in the waste to pyrolysis gas.

5.2.5 Waste Destruction Cost

Individual economic analyses were prepared for pyrolysis and incineration (with heat recovery) facilities of several different capacities for the destruction of rubber waste. An economic analysis was also prepared for the pyrolysis of an API separator bottoms waste. An economic analysis was not prepared for the pyrolysis of styrene waste because the physical form of this waste (liquid) would make it amenable to direct combustion in heat recovery equipment.

Each of these economic analyses was based on the "close coupling" of the pyrolyzer to a pyrolysis gas incinerator to preclude loss of sensible heat and condensation of high molecular weight organics in the duct between the pyrolyzer and incinerator. Each estimate was based on a system that includes waste storage, a feed system, the pyrolyzer, fume incinerator and heat recovery. However, no costs were included for air pollution control should it be required for particulates or sulfur oxides.

The quantity of each type of waste to be destroyed was based on the following estimates of waste generation from single sources:

	Source Size (Production Units)		Waste Generated (Metric tons/yr)
Refinery API separator bottoms	Crude oil capacity	50,000 bbl/day	300
Rubber Waste			
(Small Plant)	SBR Rubber	125,000 metric tons/yr	1000
(Large Plant)	SBR Rubber	250,000 metric tons/yr	2000
(From several Plants)	SBR Rubber	750,000 metric tons/yr	6000

The equipment costs for the pyrolyzer and fume incinerator plus the necessary (uninstalled) instrumentation were supplied by Surface Combustion. Other costs were estimated by ADL using the methods described in Section 3.6.

Estimated capital and operating costs are summarized in Table 5-8 (API Waste) and Table 5-9 (Rubber Waste).

TABLE 5-8. CAPITAL INVESTMENT AND OPERATING COSTS FOR PYROLYSIS OF API SEPARATOR BOTTOMS WASTE

	300 Metric tons/year
Estimated Capital Investment $ Millions	0.44
Operating Costs, $/metric ton	
Operating Labor	373.10
Auxiliary Fuel	52.80
Utilities, Chemicals, Freight	5.80
Maintenance	117.30
Capital Related Items	395.70
Credit for Recovered Heat	50.70
Total Estimated Operating Cost	894.00

TABLE 5-9. CAPITAL INVESTMENT AND OPERATING COSTS FOR PYROLYSIS OF RUBBER WASTE

	Metric Tons/Year		
	1000	2000	6000
Estimated Capital Investment $ Millions	0.67	0.92	1.50
Operating Costs, $/Metric Ton			
Operating Labor	312.90	156.30	52.10
Auxiliary Fuel	21.10	21.10	21.10
Utilities, Chemicals, Freight	5.60	5.60	4.50
Maintenance	53.60	36.80	20.00
Capital Related Items	180.90	124.30	67.40
Credit for Recovered Heat	48.10	48.10	48.10
Total Estimated Operating Cost	526.00	296.00	117.00

5.3 CHEM-TROL WASTE BLENDS INCINERATED IN A ST. LAWRENCE CEMENT KILN

In cooperation with Environment Canada and the Ministry of Environment of Ontario, the United States Environmental Protection Agency supplemented the Canadian studies through participation in analyses of samples acquired from various streams during test burns of chlorinated hydrocarbons in the St. Lawrence Cement Co. wet process kiln. The purpose of these tests was to determine whether chlorinated organic wastes could be burned in a cement kiln without adverse effects on either the environment or the cement product. It is currently common practice to add chlorides to some cement kilns in order to reduce the alkali content of the cement product. By burning chlorinated hydrocarbons both the chlorine and energy are recovered from the waste, thus reducing the cement plant's need for chlorides and fuel oil.

Testing and sampling were performed by the Ontario Research Foundation (ORF) in cooperation with St. Lawrence personnel. Three chlorinated waste blends were supplied for these tests by Chem-Trol Pollution Services, Inc. of Model City, New York. These were generally categorized as chlorinated aliphatics, chlorinated aromatics, and polychlorinated biphenyls (PCBs). Samples from the latter two tests were received by TRW for analysis.

5.3.1 Process Description

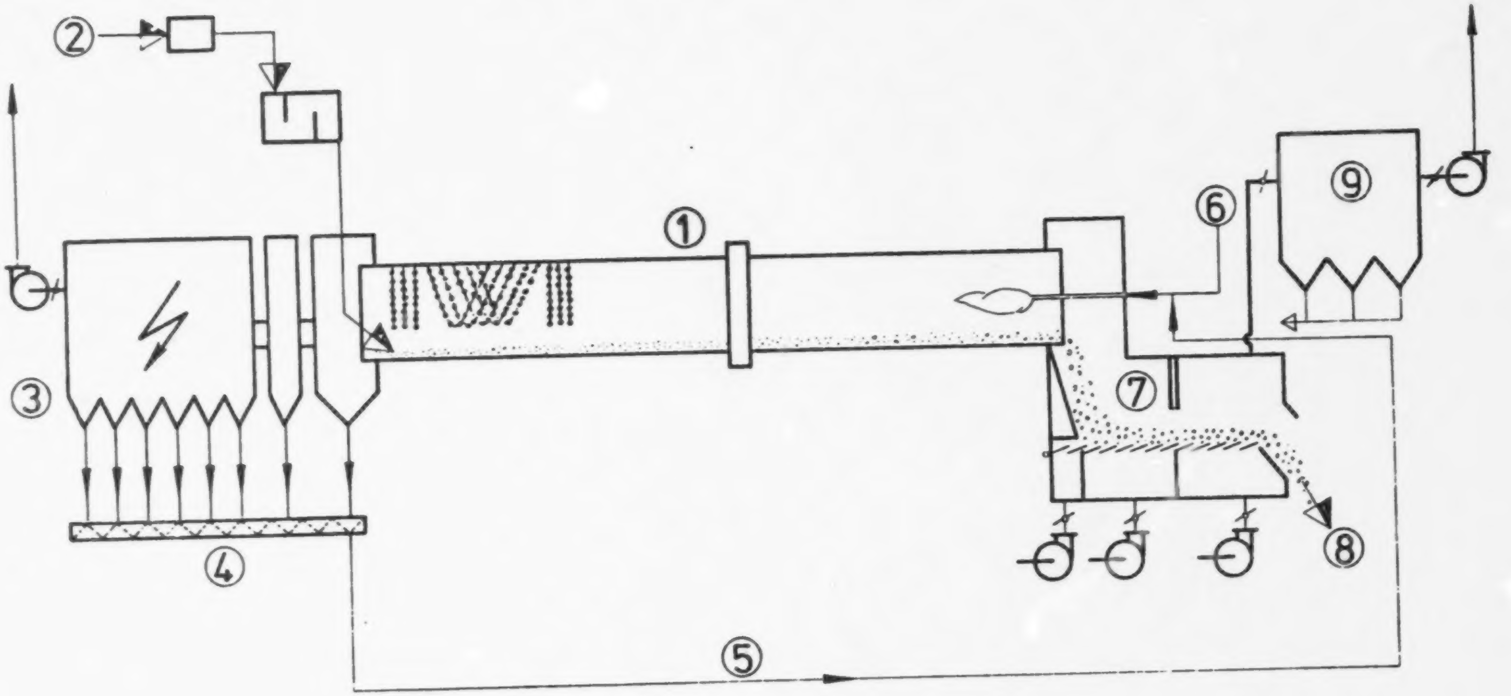
The St. Lawrence Cement Co., Mississagua Plant, has a nominal production capacity of 1,600,000 metric tons per year. The company operates two wet process kilns and one dry process suspension preheater kiln. Each of the two wet process kilns is 124 meters long with a diameter of 3.5 meters and has a nominal capacity of 950 metric tons per day (see Figure 5-3). The chain system in the drying zone consists of 52 metric tons of loosely hung carbon steel chains with a radiation curtain at the front (flame end) constructed of stainless steel chains. The chain system extends through 27 meters of kiln length. The slurry feed system is a bucket wheel conveyor with a variable speed drive taking slurry from a constant level box. Gases from each kiln (maximum capacity 4,250 m^3/min. at 230°C) pass through a six-section electrostatic precipitator. Gases from the precipitators are exhausted via a common stack 170 meters in height with an inside diameter at the exit of 4 meters. Number 6 fuel oil is burned in a single burner at the center of the burner pipe. For these tests, chlorinated hydrocarbons were fed just above and to one side of center using different size nozzles for proper atomization at different flow rates.

5.3.2 Test Description

5.3.2.1 Wastes Tested

Chlorinated Aromatics

The aromatic waste was a dark brown, low viscosity liquid that was visually free of sediment. Its measured physical characteristics were a viscosity of 1.09 centistokes (at 28°C), a specific gravity of 1.28 (at 16°C), and a gross heat content of 5170 kcal/kg (9310 Btu/lb). The waste



1-KILN
2-SLURRY FEED
4-PRECIPITATOR DUST SCREW
3-PRECIPITATOR
5-DUST RETURN

6- FUEL
7- CLINKER COOLER
8- CLINKER
9- FILTER

Figure 5-3. St. Lawrence Wet Process Cement Kiln Schematic (Courtesy of St. Lawrence Cement Co.)

blend contained 44 percent carbon, 3.5 percent hydrogen, and 49 percent chlorine. Sulfur and nitrogen contents were relatively low at 190 and 280 ppm, respectively.

The principal organic constituent was o-chlorotoluene and a complete characterization of the waste is presented in Table 5-10. These results reflect the fact that in the course of performing the tests at SLC the waste feed tank was not emptied between wastes. Thus the material for the "aromatic" burns contains ~33% chlorinated aliphatics carried over from the previous burn. The low ash content of the waste (0.02%) was composed mainly of Ba, Fe, Na, P, S, Si, and Ti.

Polychlorinated Biphenyls (PCBs)

The PCB waste was a medium brown, low viscosity liquid with fine suspended particulate that tended to float to the top and cake out on the sides of the container. Its measured characteristics were a viscosity of 5.87 centistokes (at 38°C), a specific gravity of 1.20 (at 16°C), and a gross heat content of 6710 kcal/kg (12,083 Btu/lb). The waste contained 58 percent carbon, 5.2 percent hydrogen, and 34 percent chlorine. Sulfur and nitrogen contents were 0.12 and 0.018 percent, respectively. The PCB waste composition also showed the effect of previous waste material left in the feed tank. It was composed of 12% chlorinated aliphatics, 33% chlorinated aromatics, and 45% PCBs, as shown in Table 5-11. There were 22 separate PCB compounds identified including several isomers of each of the multiple chlorinated biphenyls. The PCB waste feed also contained a small amount of ash (0.1%) which was composed primarily of Fe, Na, P, Pt, and Si.

5.3.2.2 Sampling Methods

All sampling at the St. Lawrence Cement Company tests was conducted by ORF, following methods that differed significantly from those used on other tests in this program (as described in Section 3). To sample the stack emissions from the test burns of the Chem-Trol waste blends, two trains were operated simultaneously. One of these was a standard EPA Method 5 train and the other was a low flow rate train designed by ORF which utilized Chromosorb 102 in sorbent traps for organic species. Samples were also taken of the clinker product, clinker fines, electrostatic precipitator discard dusts, and cement mixes.

5.3.2.3 Analysis Methods

The analytical methods used were those described in Section 3.3 with additional emphasis given to the types of low molecular weight chlorinated hydrocarbons that were expected by the Canadian researchers as potential partial combustion products.

5.3.2.4 Test Procedures

Test procedures were selected and carried out by the previously named Canadian groups involved in these tests and are described in Environment Canada's final report (Reference 14).

TABLE 5-10. ORGANIC COMPOSITION OF AROMATIC WASTE BY GC/MS

Compound	Estimated Concentration (% w/w)
Acetone	1.6
Methylacetate	0.3
Dichloromethane	0.4
Chloroform	11.1
Carbon Tetrachloride	13.9
Dichloroethane	3.1
Trichloroethane	2.5
Tetrachloroethane	0.4
Trichloroethylene	1.0
Toluene	1.0
Chlorotoluene	52.5
Dichlorotoluene	4.6
Dimethyl Benzene (Xylene)	0.9
Octachlorocyclopentene	3.7
$C_{10}Cl_8$ (Octachloronaphthalene)	3.0

TABLE 5-11. ORGANIC COMPOSITION OF PCB WASTE BY GC/MS

Compound	Estimated Concentration (% w/w)
Water	0.7
Acetone	1.3
Methylacetate	0.5
Methanol	0.4
Chloroform	1.4
Carbon Tetrachloride	6.8
Ethanol	5.2
Dichloroethane	0.6
Trichloroethane	0.7
Hexachloroethane	0.2
Trichloroethylene	1.6
Tetrachloroethylene	0.2
Xylenes	2.3
Toluene	1.0
Chlorotoluene	17.2
Dichlorotoluenes	2.4
Trichlorotoluenes	3.3
Octachlorocyclopentene	4.0
Chlorobiphenyl	0.5
Dichlorobiphenyls	8.4
Trichlorobiphenyls	15.5
Tetrachlorobiphenyls	11-15
Pentachlorobiphenyls	2-6
Hexachlorobiphenyls	1-2
Heptachlorobiphenyls	0.5
Octachlorobiphenyls	0.2
Di-n-octyl or Di-ethyl Hexyl Phthalate	4.0
$C_{10}Cl_8$ - Octachloronaphthalene	2.5

5.3.3 Test Results

Analysis of the flue gas samples for organic composition gave the following results:

- Hydrocarbons were not detected at significant levels in the samples of flue gas with detection limits ranging from 0.6 mg/m^3 to 0.009 mg/m^3.
- Low molecular weight chlorinated organic compounds such as methylene chloride, chloroform, and carbon tetrachloride were specifically sought by gas chromatography with electron capture detection (ECD) but were generally not detected in most of the samples. Four samples indicated the possible presence of some of these compounds, but all at levels of less than 0.1 mg/m^3 of flue gas.
- Polychlorinated biphenyls were sought by GC/ECD and GC/MS but were not found in any samples at the GC/MS detection limit of 3 $\mu g/m^3$ of flue gas.

Trace metal concentrations in the flue gases, as determined in the samples taken with the EPA sampling train, were all very low ($<10\ \mu g/m^3$) with the exception of lead in the PCB waste blend tests. The emission of lead during the PCB waste blend tests averaged 0.12 mg/m^3.

Analysis of the clinker product and discard dust samples for organic composition gave the following results:

- Hydrocarbons were not detected in solvent extracts of any of the clinker product or discard dust samples. The level of detection by GC/ECD was 5 $\mu g/g$ of sample or lower.
- Polychlorinated biphenyls were not detected in any of the clinker or dust samples by GC/ECD. Detection limits for PCBs in the samples were typically 0.04 $\mu g/g$ or better.

5.3.4 Interpretation of Results

TRW's report on this site contained only the analytical results. Environment Canada and ORF then assembled all the test data, including TRW's, and drew conclusions regarding the overall results obtained (Reference 14). In general, the TRW data indicated that there were no detectable levels of organic waste constituents in either effluent or solid samples and that there were no significant differences in any of the samples, caused by addition of the chlorinated hydrocarbon wastes to the wet process cement kiln. Organic combustion efficiencies were calculated by ORF and were reported as 99.989 percent for the chlorinated aromatic waste burns and as 99.986 percent for the waste burns containing PCBs.

5.4 SYSTEMS TECHNOLOGY - FLUIDIZED BED COMBUSTION OF PHENOL AND METHYL METHACRYLATE WASTES

Systems Technology Corporation (Systech) in Franklin, Ohio, contracts the use of a commercial fluidized bed incinerator. The Systech Waste Treatment Center in adjacent to the Franklin Solid Waste and Fiber Recovery Plant, operated by Black Clawson. Systech had an exclusive contract with Black Clawson for the destruction of liquid wastes in the fluidized bed reactor. This plant was designed and constructed under a Demonstration Grant from the Office of Solid Waste, U.S. Environmental Protection Agency. In continuous operation since 1971, the plant has met the complete waste disposal requirements of the city of Franklin.

At Black Clawson's request, two months after completion of these tests, Systech stopped incinerating liquid industrial wastes in the fluidized bed reactor. This request was made because some of Systech's waste caused operating problems which included:

- Disintegration of the sand bed, apparently due to the thermal effect of injecting liquid directly into the bed.
- Abnormal buildup of multilayered, multicolored crust on the wall of the reactor in the vicinity of the freeboard/bed interface.
- Buildup of ash of an abnormal physical character in the duct work leading from the reactor to the scrubber.
- Defluidization of the bed due to agglomeration and to contamination by chunks of the deposits described above.

Systech believed that defluidization of the bed or abnormal crust or ash buildup would not develop during the incineration of the wastes tested during this program. Some depletion of the bed sand was observed during these tests, however, during which high water content wastes were injected directly into the bed.

The two wastes tested at the Systems Technology facility, an aqueous methyl methacrylate monomer waste and an aqueous phenolic waste, were selected on the basis of their suitability for the fluidized bed reactor. The methyl methacrylate waste is a flammable liquid. Its vapor is heavier than air and may travel a considerable distance to a source of ignition and flash back. Also, at elevated temperatures, such as in fire conditions, polymerization may take place. For these reasons the fluidized bed incinerator, with its nearly isothermal conditions and lower operating temperature, was considered to be well-suited for the destruction of the methyl methacrylate waste. The aqueous phenol waste is a viscous liquid with a large volume of suspended solids and contains over 85 percent water.

The fluidized bed incinerator was selected for the destruction of the aqueous phenol waste because of (1) its ability to handle suspended solids and (2) its lower operating temperature resulting in lower thermal energy requirement for converting the water contained in the waste to steam at the incineration temperature. An additional consideration was that both the aqueous methyl methacrylate waste and the aqueous phenol waste were readily available at the Systems Technology facility.

5.4.1 Process Description

This fluidized bed reactor was selected for the program as a modern, well-instrumented incinerator of commercial capacity and design. The reactor facility, shown schematically in Figure 5-4, has an input feed rate of up to 1,360 liters per hour of high heat content liquids (over 5,560 kcal/kg) and up to 7,570 liters per hour of liquids with a heat content of 1,670 kcal/kg. Municipal wastes are burned at a maximum rate of 135 metric tons in 24 hours. Heat release capability is 15 million kcal/hr. The fluidized bed system is equipped with a venturi scrubber to control particulate emissions.

5.4.1.1 Fluidized Bed Reactor

Manufactured by Dorr-Oliver, the reactor has an inside diameter of 7.6 meters and a height of 10 meters. The silica bed is 1 meter deep at rest, expanding up to about 1.8 meters when fluidizing air is passed through the bed. Waste and auxiliary fuel are injected radially into the bed and reacted at temperatures from 600° to 810°C. Further reaction occurs in the reactor freeboard volume above the bed at temperatures up to 980°C. Construction is of carbon steel with refractory lining.

5.4.1.2 Air and Fuel Feed Systems

A fluidizing air blower provides a maximum of 440 m^3/min of air to fluidize the bed. Additional combustion air of up to 115 m^3/min is supplied to overbed air nozzles by the same blower.

Liquid wastes were pumped directly from a tank truck into the reactor by a recirculating pump system supplied by Systech. Wastes were injected radially into the reactor bed through a single 9.5 mm diameter nozzle. Flow rates were determined by recording waste liquid level changes in the calibrated tanker as a function of time.

Auxiliary fuel (No. 2 fuel oil) was fed radially into the bed through 10 bed nozzles manifolded around the reactor circumference. A maximum of 18 bed guns are available, but this number is not normally used. Fuel oil flow was measured by a flow totalizer (total volume meter) in the feed line, and verified by recording oil tank liquid level versus time.

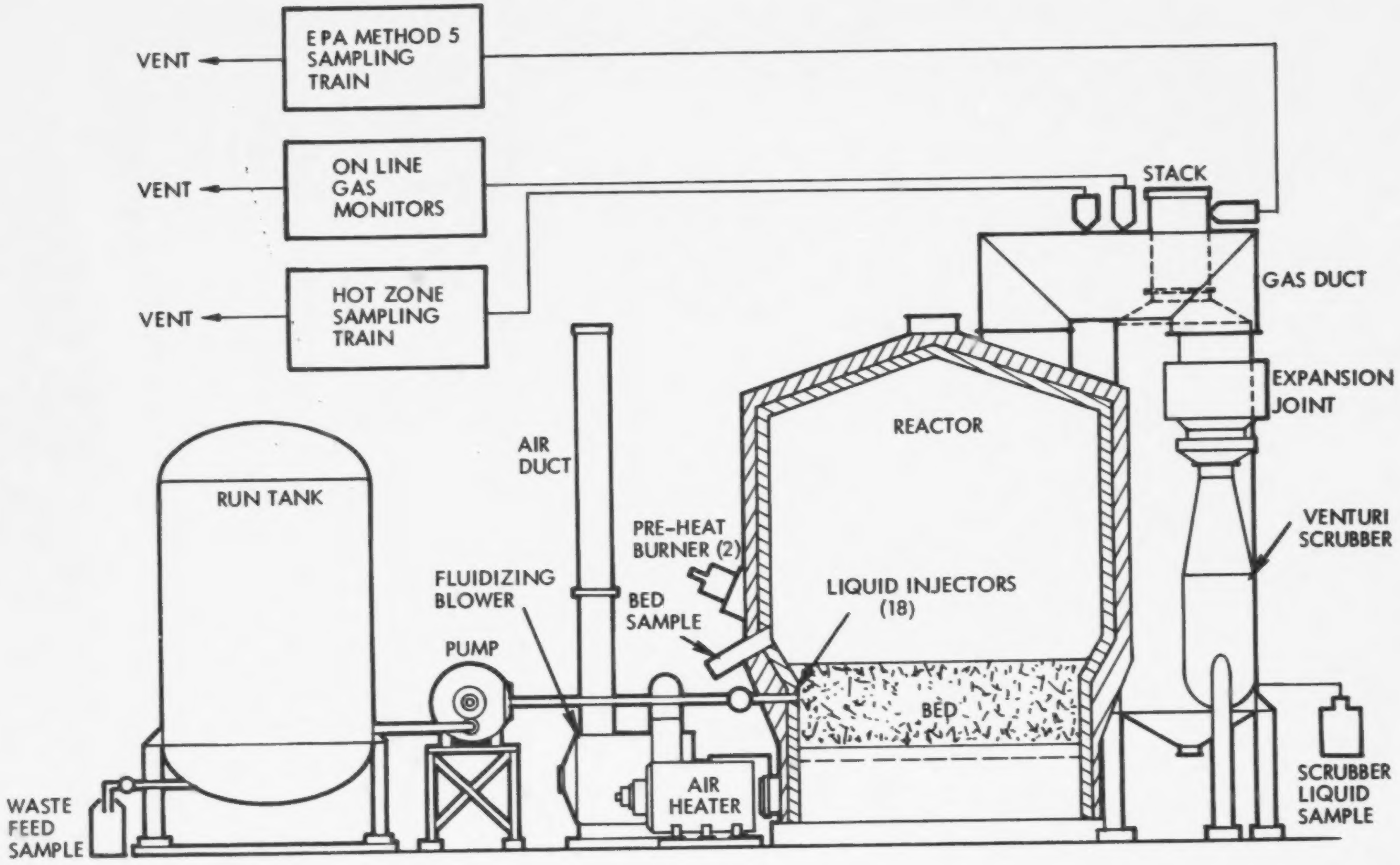

VENT
EPA METHOD 5 SAMPLING TRAIN
VENT
ON LINE GAS MONITORS
VENT
HOT ZONE SAMPLING TRAIN
STACK
GAS DUCT
EXPANSION JOINT
REACTOR
AIR DUCT
RUN TANK
PRE-HEAT BURNER (2)
VENTURI SCRUBBER
FLUIDIZING BLOWER
BED SAMPLE
LIQUID INJECTORS (18)
PUMP
BED
AIR HEATER
SCRUBBER LIQUID SAMPLE
WASTE FEED SAMPLE

Figure 5-4. Systech Fluidized Bed Facility Schematic

5.4.1.3 Instrumentation

Instruments were calibrated by Black Clawson personnel prior to initiation of testing. Measurements were made of all process parameters, including pressures, temperatures, and flow rates. On-line measurement of oxygen content in the exhaust stack was also conducted by the Black Clawson personnel.

5.4.1.4 Emission Controls

Atmospheric emissions from the combustion of liquid wastes during the Systech incineration tests were controlled by a venturi scrubber. Recirculating water is injected into the venturi to scrub particulate matter from the combustion gas stream and quench the gas temperature from ~820° to ~80°C prior to emission into the atmosphere through the stack. Spent scrubber liquid is sent to the Miami Conservancy District Wastewater Treatment Plant (adjacent to the incinerator) for processing.

5.4.2 Test Description

5.4.2.1 Wastes Tested

Phenol Waste

The phenol waste is generated from the scrubbing of gasoline with caustic to remove hydrogen sulfide and phenol, and is a major waste stream from petroleum refineries. Due to the size of the petroleum refining industry, this phenol waste stream is estimated to be generated at a rate of over 50 million kilograms per year.

The phenol waste was a greenish-black opaque liquid with a large amount of suspended solids. It had a strong phenol odor with an accompanying odor resembling that of crude oil. The waste had a specific gravity at 15°C of 1.062 and was determined to be 86 percent water. The elemental composition of the phenol waste was approximately 5.9 percent carbon, 10.5 percent hydrogen, 0.10 percent nitrogen, 0.5 percent sulfur and 0.07 percent halogens (as chlorine) with a balance being oxygen. Heat content of the phenol sludge could not be determined due to the high water content but is probably less than 1500 kcal/kg.

The organic portion, that part of the representative waste which was not water or solids, consisted of about half phenol with cresols and substituted benzenes making up most of the remaining organics. The concentration of the organic constituents in the waste, as determined by GC/MS, is shown in Table 5-12. Qualitative analyses found evidence of other organic compounds which were not volatile enough to elute from the GC column. These were identified as p-cresol, methyl esters of various carboxylic acids, and sulfur containing hydrocarbons such as sulfides, diathianes and trithianes.

Upon ashing, the phenol waste was found to contain 5.5 percent inorganic solids. The major elements present were S, Na, and Fe along with some Ca, Si, Al, K, Mg, and P.

TABLE 5-12. ORGANIC COMPOSITION OF PHENOL WASTE SAMPLE

Compound	Estimated Level in the Waste Sample (Percent w/w)[a]
Ethanol	0.06
Acetone	0.07
2-Butanone (MEK)	0.05
Butanol	<0.01
2-Ethoxyethanol	0.07
Toluene	0.3
Xylene (two isomers)	0.6
Isopropyl benzene	0.8
Phenol	3.7
o-Cresol	0.9
m-Cresol	1.9

[a] Sample contained 86 percent water and approximately 5.5 percent nonignitable solids.

Methyl Methacrylate (MMA) Waste

The methyl methacrylate waste is generated from the manufacture of acrylic plastic material, such as Lucite and Plexiglas. Methyl methacrylate wastes are also generated from the manufacture of surface-coating resins, such as latex paints, lacquer resins, and enamel resins. It is estimated that the methyl methacrylate waste is generated at the rate of 1 to 10 million kg per year.

The MMA waste was a medium brown liquid with a gritty sediment that tended to settle out of solution. The waste also had two liquid phases which at least partially separated on standing. It had a strong pungent odor characteristic of acrylic acid compounds. The waste had a viscosity of 1.42 centistokes at 37°C, a specific gravity of 1.016 at 15°C, and contained 38 percent water. The elemental composition was 38 percent carbon, 9.5 percent hydrogen, 0.06 percent nitrogen, 0.08 percent sulfur, and 0.73 percent halogens (as chlorine) with the remainder being oxygen. Heat content could not be measured on this waste either and is similarly believed to be less than 1500 kcal/kg.

The organic composition of the MMA waste is shown in Table 5-13. The sample for this analysis was taken from the waste feed tank at Systech and contained a larger number of constituents than a sample procured before the test burn. Notable among these additional constituents were a considerable amount of phenol and cresols. Their presence is most likely due to cross contamination from the phenol waste tests. Since the run tank containing the methyl methacrylate waste had just previously been used for the phenol waste run tank, it is possible that some residual, phenol-rich sludge may have remained in the tank.

The MMA waste sample contained 1.7 percent inorganic solids which consisted primarily of sodium, sulfur, and titanium. Al, Ca, Pb, and Si were also present at greater than 100 ppm concentrations.

5.4.2.2 Sampling Methods

Procedures used were those specified in Section 3.3 with the following modifications:

- Special fittings were fabricated to allow a back purge of the probe with purified compressed air while the combustion zone sampling train was not in operation. This eliminated the possibility of contamination from organic, partial combustion products produced during start-up and shutdown of the incinerator.

TABLE 5-13. ORGANIC COMPOSITION OF METHYL METHACRYLATE WASTE SAMPLE

Compound	Estimated Levels (percent w/w)[a]
Methanol	4.9
Acetone	0.7
Methylene chloride	0.7
2-Butanone	1.1
Methyl propanoate	0.4
Methyl methacrylate	33.9
2-Ethoxy ethanol	0.4
Toluene	1.1
Xylene	0.9
2-Ethoxy ethyl acetate	0.4
Phenol	12.6
Cresols	3.4

[a] Sample contains 38 percent water and approximately 1.7 percent nonignitable solids.

- The stack gases were sampled at a single point of average velocity because of vortex flow conditions at the sampling site.
- Oxidizing agents (H_2O_2 and $(NH_4)_2S_2O_8$) were added to the stack train impingers to aid scrubbing of trace metals.

Scrubber water samples were taken from a tap in the scrubber recirculation line. Prior to each test the scrubber system was filled with city water, cycled through the scrubber system and then drained. The system was then filled and circulated again before the fresh scrubber water sample was taken. The spent scrubber water was sampled immediately after the test was concluded. The sample was taken from the same tap with the recirculation pump still operating in order to maintain mixing and prevent sedimentation. The sample of sand from the bed was taken approximately one half hour after each test was concluded. The effect of the fluidizing air was considered adequate to have thoroughly mixed the sand during the test.

5.4.2.3 Analysis Methods

Procedures used were those specified in Section 3.3.

5.4.2.4 Test Procedures

Waste flow rates were selected for each test to evaluate the effects on destruction efficiency, if any, of varying the waste/auxiliary fuel volumetric flow rate ratios between 2:1 and 3:1. Air and auxiliary fuel flow rates were held essentially constant to maintain a fluidized bed temperature between 760° and 815°C.

Target test conditions for each waste were:

- Fluidizing air flow rate - 425 m^3/min
- Auxiliary fuel flow rate - 15 liters/min
- Waste flow rate - 30 to 50 liters/min
- Average bed temperature - 760° to 815°C

5.4.3 Test Results

A summary of the test results is presented in Table 5-14, beginning with the range of test conditions for each waste, including combustion temperature, residence time, and waste feed rate. The summary presented in this table also covers analytical results from samples taken during testing, destruction efficiency calculations based on those results, and costs for commercial application of the Systech incineration system. These areas are discussed further in the following sections.

TABLE 5-14. SYSTECH RESULTS SUMMARY

	Phenol Waste	Methyl Methacrylate
Bed Temperature, Average (^{o}C)	740-757	774-788
Freeboard Temperature (^{o}C)	813-899	824-843
Residence Time (sec)	12-14	12
Waste Feed Rate (liter/min)	34-50	30-36
Waste/Auxiliary Fuel* (liter/liter)	2.3-3.0	2.0-2.6
Quality of Stack Emissions:		
Particulate (mg/m^3)	1280-1430	560-630
Trace Metals (mg/m^3)	0.44-0.87 Pb	0.55-2.2 Pb
Quality of Combustion Gas:		
Total Organics (mg/m^3)	7.0-7.6	7.5
Waste Content (mg/m^3)	Not Detected (<0.03)	Not Detected (<0.16)
Trace Metals (mg/m^3)	1.0-1.2 Pb	0.85-4.7 Pb
Quality of Scrubber Water:		
Total Organics (mg/liter)	Not Detected (<0.4)	Not Detected (<0.2)
Trace Metals (mg/liter)	0.50-2.7 Pb	0.45-1.8 Pb
Quality of Ash (Fluidizing Sand):		
Waste Content (mg/kg ash)	Not Detected (<0.2)	Not Detected (<1.0)
Destruction Efficiency:		
Total Organics (percent)	99.93-99.95	99.96-99.98
Waste Constituents (percent)	>99.999	>99.999

*No. 2 oil utilized as auxiliary fuel for all tests.

5.4.3.1 Incinerator Operating Conditions

The first phenol waste test consisted of feeding the waste at a ratio of 3.0:1 to the auxiliary fuel with a residence time of 14 seconds. The second phenol test used a lower waste to auxiliary fuel ratio (2.3:1) and a shorter residence time of 12 seconds. The two test burns of MMA waste were conducted at waste to fuel ratios of 2.0:1 and 2.6:1, and both had a residence time of 12 seconds. Temperatures in the reactor bed ranged from 720° to 790°C and in the freeboard area above the sand bed from 790° to 900°C. The pressure drop across the fluidized bed was approximately 80 cm H_2O, and the gas pressure in the freeboard area was 9 to 18 cm H_2O.

5.4.3.2 Characterization of the Incineration Process

Percent oxygen in the freeboard area for the two phenol and two MMA tests was 10.7 and 12.6, 13.4 and 11.6, respectively. Similarly the carbon dioxide concentrations were 9.4 and 7.6 percent, and 7.4 and 8.0 percent. Freeboard gas concentrations did not exceed 25 ppm of CO, 55 ppm of NO_x, or 40 ppm of total hydrocarbons (as methane).

Analysis of samples taken of the freeboard gas found no evidence of any waste constituents above the detection limits of 0.007 mg/m^3 for phenol and 0.04 mg/m^3 for MMA. Total amounts of nonhazardous organic materials found averaged 7.5 mg/m^3. Levels of heavy metals were generally low with only lead being present at levels above 1 mg/m^3.

Particulate loadings in the stack were 710 mg/m^3 for the background burn on No. 2 oil, 560 and 630 mg/m^3 for the MMA waste burns, and 1300 and 1400 mg/m^3 for the phenol waste burns. Most of the particulate consisted of fine sand particles disintegrated from the fluidizing bed by direct injection of these high water content wastes. Stack emission levels for all toxic metals were less than 0.2 mg/m^3 except for lead emissions which reached 0.8 mg/m^3 for the phenol tests and 4.5 mg/m^3 for the MMA tests.

None of the waste constituents were found in the scrubber water samples above a detection limit of 1 mg/liter, and no significant changes in trace metal concentrations were found. No traces of waste compounds were found in the bed sand samples either at detection limits of 1 mg/kg for MMA and 0.2 mg/kg for phenol.

5.4.4 Interpretation of Results

Incineration of each waste was accomplished with high efficiencies in the fluidized bed reactor. Waste destruction efficiencies were over 99.999 percent for each test. The total organic destruction efficiencies for the waste tests were 99.93 to 99.98 percent and 99.85 percent for the background test. Destruction efficiency for total organics compares the input rate of combined waste and auxiliary fuel to emitted rate of all organic material found both in the combustion zone samples and by the on-line hydrocarbon monitor. Waste destruction efficiency compares only waste input rate to concentration of organic waste constituents in the combustion gas. In addition to the fact that the waste constituents could not be detected in the combustion gas, scrubber water, or sand, no significant evidence of any toxic by-products of the waste destruction, such as polynuclear organic materials was found.

5.4.5 Incineration Costs

Capital and operating cost estimates prepared for fluidized bed reactor-venturi scrubber systems to destruct each of the two wastes are summarized in Table 5-15. Capital investment, not including land costs, for a facility to incinerate 13.2 million liters/yr of aqueous methyl methacrylate is approximately six million dollars, with an operating cost equivalent to $242/metric ton of waste destructed. A facility to incinerate 22.8 million liters/yr of aqueous phenol waste would also require a capital investment of six million dollars, less land costs, and an operating cost of $140/metric ton. Costs for both facilities were estimated based on using the same size reactor as Systech's, with the MMA waste disposal site being a commercial facility located within 150 miles of the waste generating plant and the phenol waste being disposed on-site at the refinery.

TABLE 5-15. CAPITAL INVESTMENT AND OPERATING COSTS FOR FLUIDIZED BED COMBUSTION OF METHYL METHACRYLATE WASTE AND PHENOL WASTE

	Methyl Methacrylate 13,200 cu m/year	Phenol 22,800 cu m/year
Estimated Capital Investment $ Millions	5.98	6.07
Operating Costs, $/metric ton		
Operating Labor	9.30	6.60
Auxiliary Fuel	35.70	37.50
Utilities, Chemicals, Freight	38.30	6.30
Maintenance	36.30	21.30
Capital Related Items	122.40	68.80
Total Estimated Operating Cost	242.00	140.00

5.5 ZIMPRO - WET AIR OXIDATION OF COKE PLANT AND AMIBEN® WASTES

Wet air oxidation was selected as a method for testing in this program because it offers the potential for thermal treatment of wastes with low heating values, such as aqueous streams containing low concentrations of organic materials. The objective of this program was to evaluate the capabilities of commercial scale facilities. However, a full-scale wet air oxidation facility could not be located within the continental United States which would be available for this test program. It was decided to conduct a series of tests using the pilot plant unit operated by Zimpro, Inc. in Rothschild, Wisconsin. Wet air oxidation tests were carried out on coke plant waste and Amiben® (herbicide) production waste.

The criteria for selection of these wastes included the following:

- The waste should be an aqueous solution containing oxidizable pollutants at concentrations too high or too toxic for biological treatment.

- The total heating value could be low (<1500 kcal/Kg, <3000 Btu/lb), precluding economic destruction by high temperature incineration.

- Substantial quantities of sulfates and chlorides could be tolerated and there were no intrinsic restrictions on elemental composition.

5.5.1 Process Description

Wet air oxidation is carried out in an aqueous medium with high pressure air at temperatures typically between 130°C (266°F) and 350°C (662°F).

Both a gaseous and aqueous stream result from wet air oxidation, and the products of destruction may be found in either stream. The major portions are expected to remain with the aqueous stream. In addition, an oxidation catalyst such as a copper compound may be required and will remain in the aqueous stream.

The Zimpro wet air oxidation system as used for this test program is shown schematically in Figure 5-5. The 25 liters of reactor volume is divided equally between two vessels so that it can fit into the trailer. The vessels are constructed of titanium so that they can handle a wide variety of chemical conditions.

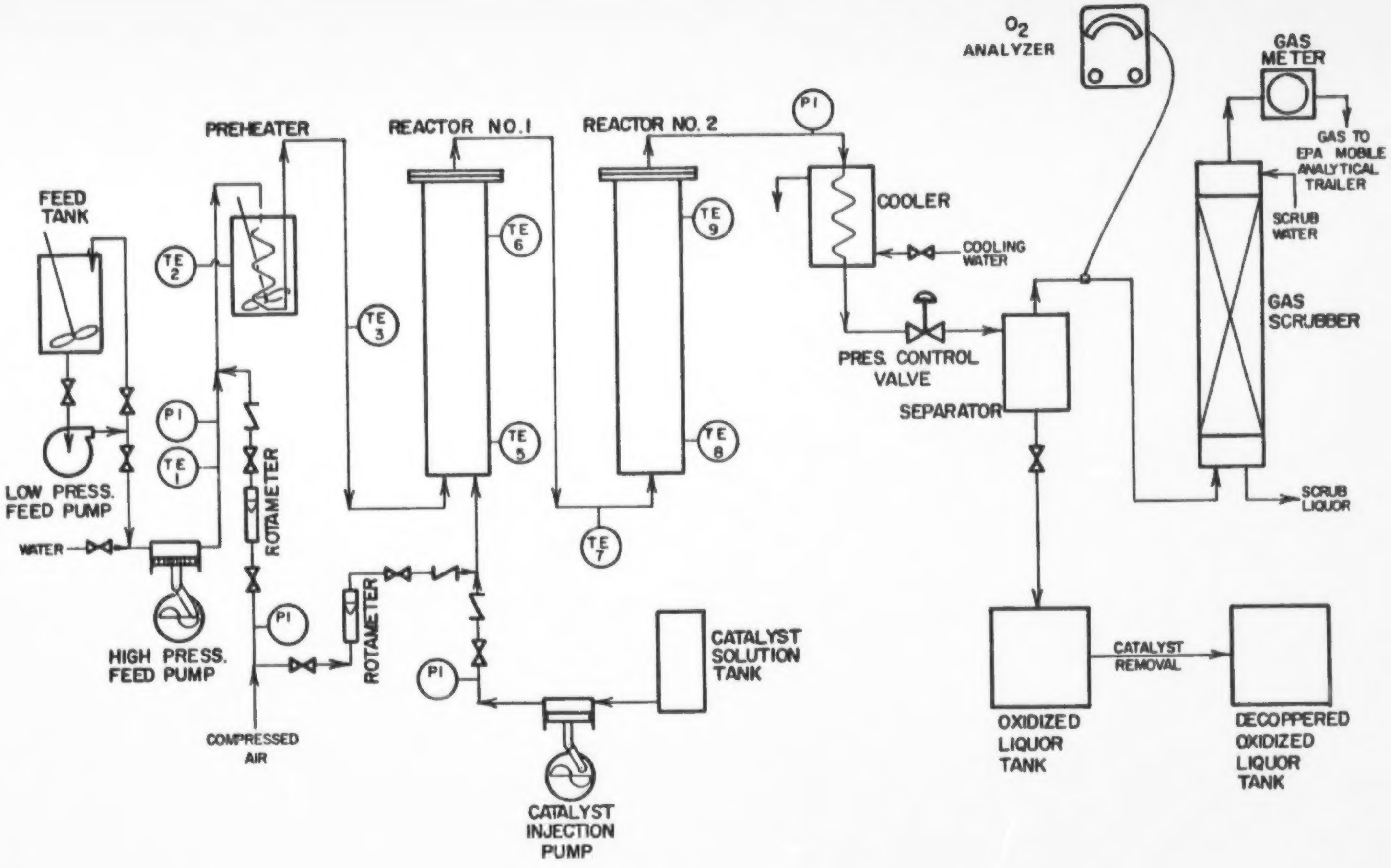

FEED TANK
LOW PRESS. FEED PUMP
WATER
HIGH PRESS. FEED PUMP
TE 1
TE 2
PI
PREHEATER
ROTAMETER
ROTAMETER
COMPRESSED AIR
PI
TE 3
REACTOR NO. 1
TE 6
TE 5
PI
CATALYST INJECTION PUMP
CATALYST SOLUTION TANK
REACTOR NO. 2
TE 9
TE 8
TE 7
PI
COOLER
COOLING WATER
PRES. CONTROL VALVE
SEPARATOR
O_2 ANALYZER
GAS METER
GAS TO EPA MOBILE ANALYTICAL TRAILER
SCRUB WATER
GAS SCRUBBER
SCRUB LIQUOR
OXIDIZED LIQUOR TANK
CATALYST REMOVAL
DECOPPERED OXIDIZED LIQUOR TANK

Figure 5-5. Flow Diagram of Mobile Industrial Pilot Plant Wet Oxidation

The test system included the following components:

- Feed tanks
- Centrifugal type feed pump
- High pressure waste pump
- High pressure catalyst injection system
- High pressure air supply
- Feed preheater
- Two reactors (in series)
- Effluent cooler
- Pressure reducing valve
- Gas-liquid separator
- Vent-gas scrubber
- Oxidized liquor storage tanks

Instrumentation included monitoring and control of temperature in the reactors, control of pressure, monitoring of percent residual oxygen in the vent gases and measuring the flow rate of the vent gases.

In operation, the aqueous waste stream containing oxidizable components is pumped from the feed storage tanks using a centrifugal pump to feed the high pressure positive displacement type pump. The waste then flows through the hot oil preheater into the wet oxidation reactors. The temperature of the incoming feed is increased to a level which will support the oxidation reaction in the reaction vessel. Most of the air required for oxidation is mixed with the waste prior to entering the hot oil preheater in the pilot plant. Catalyst solution is directly injected into the bottom of the first reactor. The reactors in the wet air oxidation process are nonmechanically agitated, vertical, trayed pressure vessels. The normal operating temperatures range from 150° to 320°C at corresponding pressures of 15 to 205 atm. As oxidation progresses through the reactor, heat is liberated, increasing the temperature of the reaction mixture. The hot oxidized effluent, comprised mainly of steam, water, carbon dioxide and nitrogen, is cooled in a heat exchanger.

Following cooling, the pressure is reduced through a control valve and the liquid and gas phases are separated. The oxidized waste then flows to product storage tanks while the gas stream is monitored by a continuous oxygen analyzer. The off-gas is sent to the scrubber and is then metered before venting to the atmosphere.

The oxidation of the wastes was carried out using a copper base catalyst. The catalyst was removed from the oxidized liquor by sulfide precipitation. In the Amiben® waste test, the aqueous effluent was subjected to an additional process operation, solvent extraction. The vent gases were scrubbed by contacting with ordinary tap water at ambient conditions.

5.5.2 Test Description

5.5.2.1 Wastes Tested

The chemical wastes selected for testing at this wet air oxidation facility were two which, based on the information supplied by the waste generators, would be difficult to treat in other types of facilities.

Coke Plant Waste

The coke plant waste was a clear, light brown, aqueous solution with a few flecks of black particulate materials. The total dissolved solids contents was <1%, of which 5-10% was organic material. Major components and their concentrations are given in Table 5-16. Elements present in the waste at trace levels (1-10 ppm) were: potassium, 7 ppm; iron, 6.5 ppm; magnesium, 4 ppm; fluorine, 2 ppm; silicon, 2 ppm; and copper, 1 ppm. Calcium, sodium, and phosphorus were found at concentrations >10 ppm. None of these species were expected to be significantly affected by wet air oxidation and none of them were of concern at the concentrations present in the waste.

The higher heating value of the waste was estimated at <55 kcal/Kg (100 Btu/lb).

Amiben® Waste

Two Amiben® wastes were available, taken before and after "well pretreatment." The two wastes were essentially the same except for pH, and it is understood that the well treatment is simply a neutralization and some filtration. The "before," or basic, Amiben® waste was chosen because the wet oxidation process will produce some acids and thus partially neutralize the basic waste. All data in this report pertain to the basic, before treatment, Amiben® waste.

The waste was a clear, amber aqueous solution with a total solids content of 6-7% and an ash content of 3.6%. The organic content was therefore about 3-3.5%. Major components and their concentrations are also given in Table 5-16. The results of SSMS analysis indicate that the only trace elements present in the waste at concentrations >1 ppm were: calcium, 44 ppm; iron, 33 ppm; phosphorus, 12 ppm; silicon, 4 ppm; titanium, 3 ppm; fluorine, 2 ppm; and iodine, 2 ppm. None of these species is expected to be significantly affected by the wet air oxidation process, and none of them is especially toxic at the concentrations present in the waste.

5.5.2.2 Sampling Methods

Samples were collected over a three-hour period during steady-state operation for each waste. The types of samples taken were:

- Bulk samples of aqueous waste feed, aqueous reactor effluent, scrubber water feed and spent scrubber water.

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TABLE 5-16. PRINCIPAL COMPONENTS OF COKE PLANT WASTE AND AMIBEN® WASTE

Component	Concentration	
	Coke Waste (mg/liter)	Amiben® Waste (g/liter)
Organic Species		
Phenol	743*	
Cresol	188*	
Quinoline	38	
Indole	41	
Aniline	26	
2,5-Dichloro-3-nitrobenzoic acid		3.1
2,5-Dichloro-6-nitrobenzoic acid		16.0
Inorganic Species		
pH	8.8	12.1
Cl^-	3560	5.67
$SO_4^=$	2910	
CN^-*	309	0.193
NH_3-N*	2410	
Collective Parameters		
BOD_5^*	2083	5.28
COD*	5520	30.5

*Asterisks indicate data reported by Zimpro, Inc. Others are ADL values.

- Sample of vent gas fed to on-line instruments for continuous monitoring of test.

- Grab samples of vent gases.

In addition, Zimpro, Inc. supplied samples of process effluents which had been treated in batch processes after the wet air oxidation.

Sampling methods used were those described in Section 3.3 with the following modifications:

- One-liter samples of liquid streams were taken at hourly intervals over the course of the 3-hour sampling period. The four samples of each stream were composited in the laboratory.

- The entire flow of vent gas from each waste test was conducted via 37 mm polyethylene tubing into the EPA trailer. A portion of this vent gas was tapped off and passed to the gas conditioning system and instruments.

- A 1.2 cm Pyrex probe was used to draw a sample through the comprehensive sampling train. The impingers contained dilute aqueous nitric acid to trap ammonia.

- A second gas grab sample was collected from the bypass line of the hydrocarbon analyzer. The bypass line was also sampled using detector tubes for hydrogen cyanide.

- An EPA Method 5 sampling procedure involving a multipoint traverse was not appropriate for this facility, since the vent gas pipe had a diameter of only 37 mm (1.5 in.) and carried a total flow of <3 cubic meters/hr (<2 cfm).

5.5.2.3 Analysis Methods

The methods used for the Zimpro samples were those described for the overall test program (Section 3.3).

5.5.2.4 Test Procedures

Tests were run following the basic procedures described in Section 3.2 with these modifications:

- Target operating conditions were determined by Zimpro, Inc., based on preliminary laboratory autoclave tests. Only one test, at the optimum condition, was used for each waste.

- The "purge" consisted of circulating clean municipal water through the reactors at the temperature and air pressure chosen for the run.

- The test run period was extended for up to 24 hours to allow Zimpro to complete its normal test procedures.
- The oxidized aqueous effluents were subjected to batch treatments following completion of the wet air oxidation test run. Both coke waste and Amiben® waste effluents were subjected to a sulfide precipitation step for removal of the copper catalyst. In addition, for the Amiben® waste a three-stage perchloroethylene solvent extraction procedure was applied to remove remaining organic products of oxidation.

5.5.3 Test Results

Table 5-17 summarizes the planned and actual test conditions for the two waste tests.

5.5.3.1 Products of Wet Air Oxidation

Both a gaseous and an aqueous stream result from wet air oxidation, and the products of destruction may be found in either stream. Table 5-18 summarizes the results of analyses of the aqueous streams and Table 5-19 presents the results of the on-line monitoring of the gaseous effluents.

TABLE 5-17. SUMMARY OF WET OXIDATION TEST CONDITIONS, PLANNED AND ACTUAL

	Coke Plant Waste		Amiben® Waste	
	Planned*	Actual	Planned*	Actual
Waste Feed Rate, liter/hr (gal/hr)	23.8 (6.3)	20.8 (5.5)	23.8 (6.3)	24.2 (6.4)
Reactor Residence Time	1 hr	~1 hr	1 hr	~1 hr
Reactor Temperature, °C	280	279	280	281
Reactor Pressure, atm	107	107	107	107
Catalyst Addition	Yes	0.3 gph	Yes	0.3 gph
Effluent Gas Vent Rate, cu m/hr (cfm)	0.8 (0.5)	2.5 (1.5)	- -	2.9 (1.7)
Excess O_2 in Vent Gas, %	12	16.3	3	8.8

*Determined by Zimpro, Inc., in laboratory scale autoclave tests.

TABLE 5-18. SUMMARY OF ANALYTICAL RESULTS FOR OXIDIZED AQUEOUS EFFLUENTS

COKE PLANT WASTE Operating Conditions 279°C (535°F) 107 Atmospheres of Pressure 1.15 Hour Residence Time				AMIBEN® WASTE 281°C (538°F) 107 Atmospheres of Pressure 1 Hour Residence Time			
Concentration mg/liter				Concentration, g/liter			
Waste Component	Feed	Effluent	% Destruction	Waste Component	Feed	Effluent	% Destruction
Cyanide	309	< 3	>99	2,5 Dichloro-6-Nitrobenzoic acid plus 2,5 - Dichloro-3-Nitrobenzoic Acid	19.1	<0.1	>99
Phenol	743	1.05	99.9				
Cresol	188	< .2	99.9				
Quinoline	38	13	65.7	BOD_5	5.28	0.90	90
BOD_5	2083	23	98.9	COD	30.5	2.92	82
COD	5520	481	91.3				
Components of Major Environmental Concern in Aqueous Effluents: Aqueous Stream: Quinoline at 13 ppm (Copper at 250 ppm)* NH_3, 2410 mg/l as N				Components of Major Environmental Concern in Aqueous Effluents: Aqueous Stream: 2,5 Dichloronitrobenzene, at 2.10 g/l (Copper at 300 ppm)*			

*The copper is added to the waste as an oxidation catalyst and is normally recovered from the process effluent.

TABLE 5-19. SUMMARY OF ON-LINE MONITORING DATA FOR GASEOUS EFFLUENTS

	Coke Plant Waste	Amiben® Waste
Hydrocarbons, ppm (as methane)	180 ± 20	750 ± 20
Carbon Monoxide, ppm	1050 ± 35	3210 ± 80
Carbon Dioxide, %	2.30 ± 0.15	12.0 ± 0.9
Oxygen, %	17.5 ± 0.3	9.1 ± 0.7
Nitrogen Oxides, ppm	0.35 ± 0.05	12.3 ± 2.2

No organic products of partial oxidation of phenol or cresol were found in the wet air oxidation process effluents. The quality of volatile hydrocarbon stripped from the oxidized waste by the vent gas corresponds to <2% of the carbon in the phenol and cresol originally present in the waste. It is possible that small quantities of highly oxidized, water soluble species such as acetic acid were present in the effluent, but these could not have been major oxidation products.

No significant amounts of potentially hazardous particulate or vapor species appeared to be present in the vent gas. The concentration of carbon monoxide in the vent gas was 1000 ppm, but no hydrogen cyanide was detected in the vent gases. The total particulate loading of the vent gas was found to be 2.73 mg/m^3.

There was no evidence of significant contamination of the scrubber water from the coke plant waste test.

For the Amiben® waste, the major criterion for evaluation of wet air oxidation was the destruction of the dichloronitrobenzoic acids in the waste feed. These species were not detectable (<0.1 g/liter) in the effluents. However, the aqueous effluent from the oxidation process contains 2.1 g/liter of dichloronitrobenzene, corresponding to 13.5% of the original quantity of nitrochlorobenzoic acids. The dichloronitrobenzene is reported to be toxic, so formation of this product is not a desirable result. However, a perchloroethylene extraction removed >99% of this specie from the process effluent.

The dramatic decrease in pH between feed and effluent is typically observed in wet air oxidation of unbuffered solutions. A somewhat surprising result of this test is that the concentration of free chloride ion does not increase above the ~5 g/liter found in the feed to correspond to the destruction of the dichloronitrobenzoic acid. Analyses by Zimpro, Inc. involving vigorous sample digestion prior to analysis indicated that the total chlorine concentration of both feed and effluent is 10.9 g/liter, so the chlorine released by oxidation is apparently remaining in solution. The possibility that substantial quantities of chlorinated organic species remain in solution but were not detected in any of the analyses is remote. At present, no conclusion can be drawn as to the speciation of the chlorine released by oxidation of dichloronitrobenzoic acid in these tests.

No potentially hazardous species appeared to be present in the comprehensive sampling train gas grab sample. The principal hazard identified in the vent gas was the high concentration of carbon monoxide of >3000 ppm. The total particulate loading of the vent gas was found to be 10.6 mg/m^3, of which 1% was organic solvent extractable.

There was no evidence of significant contamination of the scrubber water from the Amiben® waste test.

5.5.4 Interpretation of Results

Wet air oxidation is particularly well suited to the treatment of aqueous wastes containing a few percent or less of oxidizable contaminants.

Emissions to the atmosphere from wet air oxidation are generally not of significant consequence within established regulations. Aqueous effluents from wet air oxidation often can be expected to require further treatment to meet effluent limitations. Consequently, wet air oxidation systems may require minimal attention to air emissions, but will usually require subsequent water treatment for the removal of oxidation catalyst and/or the removal of residual organic substances.

For the coke plant waste, the test showed >99% destruction of phenol, cresol and cyanide in the waste, 98.9% reduction BOD, and 91.3% reduction in COD. Destruction efficiency for quinoline in the waste was only 66%, indicating that some organic species are more resistant to oxidation than phenols. Potential for adverse environmental emissions exists, since the aqueous streams from wet air oxidation contained 13 ppm of quinoline, 250 ppm copper and 2410 ppm of ammonia (as N). Removal of copper would certainly have to be achieved prior to discharge of oxidized waste to receiving waters. The removal of residual organics and ammonia would probably also be required; a number of methods such as activated carbon adsorption, ammonia stripping, and so on, might be considered. The vent gases from the scrubber, containing 180 ppm hydrocarbons and 1050 ppm carbon monoxide, can probably be emitted to the atmosphere through a stack of sufficient height so as to prevent exceeding ambient air quality standard.

For the Amiben® waste, the test showed 99.4% destruction of the 3-nitro plus 6-nitro isomers of 2,5-dichloronitrobenzoic acid, 90.4% reduction in BOD and 82.9% reduction in COD. However, 13.5% of the dichloronitrobenzoic acid was accounted for by dichloronitrobenzene in the process effluent. Potential for adverse environmental emissions exists, since the aqueous stream from wet air oxidation contained 2100 ppm of 2,5-dichloronitrobenzene, 300 ppm copper and 150 ppm of ammonia (as N). The 2,5-dichloronitrobenzene could be removed by perchloroethylene extractions; however, subsequent treatment for removal of copper, residual organics, and ammonia would probably be required as for the coke plant waste. The vent gases from the scrubber containing 750 ppm hydrocarbons and 3210 ppm carbon monoxide can probably be emitted to the atmosphere directly through a stack of sufficient height so as to prevent exceeding ambient air quality standards or could be oxidized by thermal or catalytic means.

5.5.5 Waste Destruction Cost

Individual economic analyses have been developed for the destruction of coke plant and Amiben® wastes. The quantity of each type of waste to be destroyed is based upon the following estimates of waste generation from single sources:

	Size of Production Unit	Estimated Waste Flow to be Treated
Coke plant waste	3200 tons coke/ day	2,120 cu m/day (560,000 gal/day)
Amiben® waste	-	151 cu m/day (40,000 gal/day)

The resulting liquids from wet air oxidation of coke plant and Amiben® wastes must be treated further.

ADL estimated the cost of the following treatment sequences to achieve satisfactory effluents:

Coke Plant Waste	Amiben® Waste
Wet air oxidation (including catalyst recovery	Wet air oxidation (including catalyst recovery and solvent extraction)
Ammonia removal	Neutralization
Neutralization	Biological treatment
Biological treatment	

Zimpro, Inc. provided estimates of the capital investment requirements for the wet air oxidation treatment systems which included high pressure pumps, exchangers, reactors, pressure reducing valves, gas-liquid separators, catalyst recovery and the associated instrumentation.

The cost of the other equipment, such as waste storage and ammonia stripping, was estimated by ADL using the methods described in Section 3.6.

Estimated capital and operating costs are summarized in Table 5-20.

TABLE 5-20. CAPITAL INVESTMENT AND OPERATING COST FOR WET AIR OXIDATION OF COKE PLANT WASTE AND AMIBEN® MANUFACTURING WASTE

	Coke Plant Waste 700,000 cu m/yr	Amiben® Waste 50,000 cu m/yr
Estimated Capital Investment $ Millions	10.7	2.20
Operating Costs, $/metric ton		
Operating Labor	0.35	2.50
Auxiliary Fuel	1.00	0.50
Utilities, Chemicals, Freight	0.50	1.20
Cost of Follow-on Treatment	3.30	0.30
Maintenance	0.60	1.80
Capital Related Items	4.20	11.80
Total Estimated Operating Cost	10.00	18.00

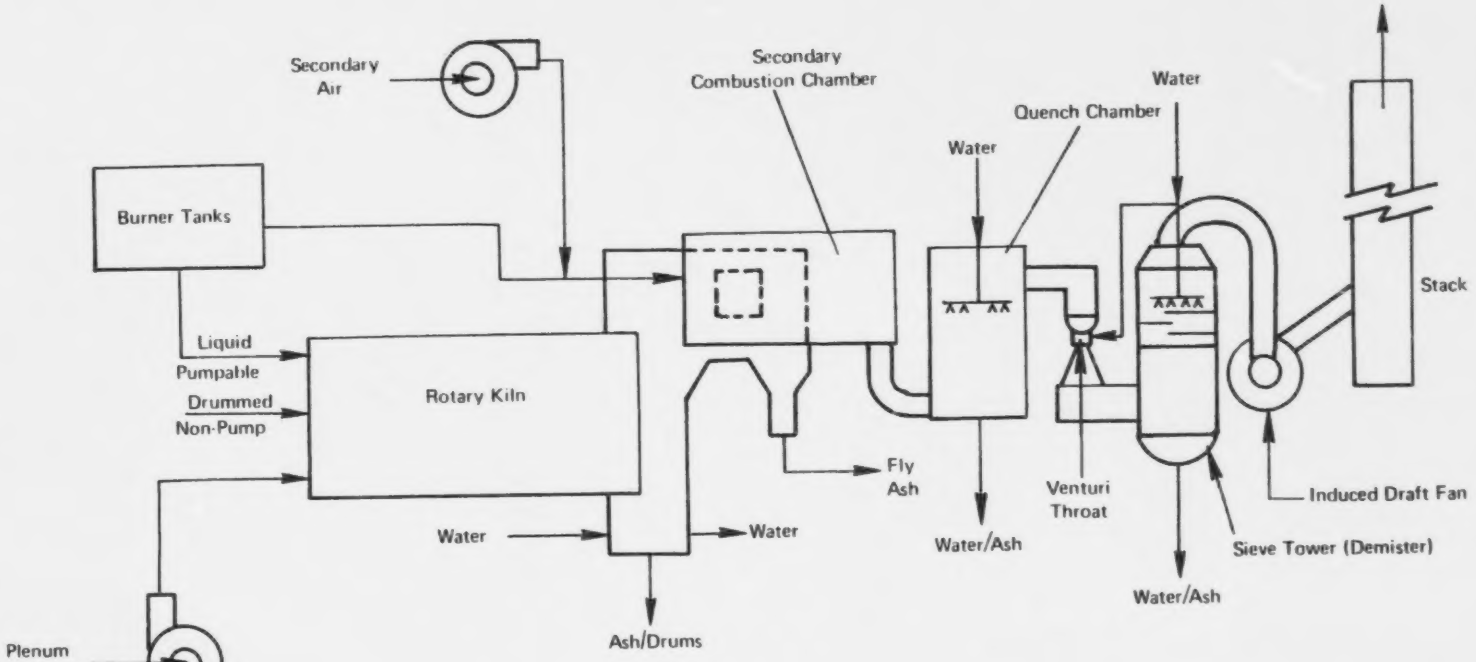
Secondary
Air
Secondary
Combustion Chamber
Water
Quench Chamber
Water
Burner Tanks
Stack
Liquid
Pumpable
Drummed
Non-Pump
Rotary Kiln
Fly
Ash
Venturi
Throat
Induced Draft Fan
Water
Water
Water/Ash
Sieve Tower (Demister)
Water/Ash
Ash/Drums
Plenum
Air

Figure 5-6. Schematic of Rotary Kiln Facility (Courtesy of 3M Company)

5.6 3M COMPANY - ROTARY KILN INCINERATION OF POLYVINYL CHLORIDE WASTE

Rotary kiln incineration was selected as a method for testing in this program because it represents a well-established technology with widespread applicability to a variety of hazardous wastes. The 3M Company Chemolite incinerator system is a large facility of this type, located in Cottage Grove, Minnesota. The waste material tested at this facility was a stream generated in the production of polyvinyl chloride.

5.6.1 Process Description

The 3M Company's Chemolite incineration system includes: the material handling building, the rotary kiln primary combustion chamber, secondary combustion chamber, air pollution control train (wet scrubber), fan, stack, and scrubber water neutralization system. The facility, which has a rated capacity of 23 million kcal/hour, is shown schematically in Figure 5-6.

The rotary kiln is fired with liquid waste which is fed through a burner at the front of the kiln. Drummed (nonpumpable) wastes are fed to the kiln via a semiautomatic system that can feed either drum contents or both drum and contents to the kiln at preset intervals. The kiln is usually operated at 815 to 870°C, with a solids detention time of about 2 hours and a combustion gas detention time of approximately 2 seconds. At the downstream end of the kiln, an ash handling system quenches and collects ash and spent drums, which are eventually trucked to an on-site landfill. Gases from the kiln flow through a mixing chamber to a secondary combustion chamber fired with pumpable waste and/or No. 2 fuel oil. The secondary chamber is generally operated at 980°C, with a gas detention time of approximately 1 second.

Effluent from the secondary chamber flows through a water quench chamber, high energy venturi scrubber, and a demister. An induced draft fan then exhausts the gases to the atmosphere through the stack. Water streams discharged from the scrubber system, demister, and ash handling system are combined into a single wastewater stream. The wastewater is neutralized with ammonia, if necessary, and is sent to a 3M Company wastewater treatment system.

Although the intrinsic capacity of the facility is large, the actual waste throughput depends on the composition and heat content of the waste. Highly combustible wastes can be fed at a rate nearly equal to the maximum capacity of the incinerator, while marginally combustible wastes must be fed at a lower rate to accommodate the additional heat input from the required auxiliary fuel.

5.6.2 Test Description

5.6.2.1 Waste Tested

The waste selected for testing at the 3M Company's Chemolite incineration system was a stream generated in the production of polyvinyl chloride (PVC). The estimated total annual production of PVC waste similar to that selected for testing is on the order of 2300 metric tons. A waste of this type was selected for testing in the program because of the possible hazard associated with the presence of residual vinyl chloride monomer. The waste was matched with a rotary kiln incinerator because the latter type of facility can readily handle wastes with high solids content.

The PVC waste was found to be 28% solids, with water accounting for most of the remainder. The solid material consisted of orange-brown, grainy particles that were roughly spherical. This material was found to be primarily polyvinyl chloride.

The representative waste sample was found to contain 220 ±55 ppm by weight (wet waste basis) of residual vinyl chloride monomer. Other organic species identified were some aliphatic hydrocarbons (predominantly unsaturated) and <0.1% by weight (wet basis) of tetrachloroethylene.

The ash content of the waste was found to be 1.7%. No trace elements were found by spark source mass spectroscopy (SSMS) at concentrations high enough to cause concern for emissions of toxic metals at the feed rates used in the tests. Calculated values of maximum possible stack gas concentrations, assuming no removal by a scrubbing system, were less than the Occupational Safety and Health Act (OSHA) standard value for all elements identified. In practice, incineration of the PVC waste would always require a pollution control system (wet scrubber) to treat the hydrochloric acid emissions.

The PVC waste, due to its high water content, had a low heating value, estimated at 740 kcal/kg. A relatively low feed rate (6 drums/hour) of waste to the kiln was required for this marginally combustible waste.

5.6.2.2 Sampling Methods

The methods used were those described in Section 3.3 with the following modifications.

- A single composite sample of waste feed was prepared. A total of about 2 kg of sample was acquired by taking approximately equal quantities of sample from each of eight drums selected at random.

- Portions of the combustion gas stream were injected at intervals into a gas chromatograph installed in the sampling trailer for these tests. This was done to verify that incinerator emissions of vinyl chloride monomer did not exceed the EPA limit (for vinyl chloride and PVC plants) of 10 ppm discharge to ambient air.

- Ambient air samples in 5-liter Tedlar® bags were taken from areas where drums of waste were stored or handled. The objective of this sampling was to verify that personnel were not exposed to concentrations of vinyl chloride monomer in excess of the OSHA standard value of 1 ppm (for 8-hour time weighted average). No detectable amounts of vinyl chloride monomer (i.e., <0.2 ppm) were found.

- A knock-out trap consisting of an oversized impinger to condense water was inserted in the combustion zone sampling train between the filter and the sorbent trap. The impingers in this train contained sodium hydroxide to collect acidic gases.

- A portion of the combustion zone effluent was collected in gas sampling bulbs from the bypass line of the hydrocarbon analyzer.

- The stack gas effluent was sampled isokinetically, according to EPA Method 5 by a traverse along one stack diameter. Concern for field team personnel exposed to low temperatures and strong winds precluded use of two perpendicular traverses.

- A sample of ash from the kiln was not acquired because there was no way to clean the ash pit prior to testing. No sample that represented residue from these tests only could be obtained.

5.6.2.3 Analysis Methods

The methods used for analysis of the 3M Company samples were those described in Section 3.3. Analysis of vinyl chloride monomer was performed by gas chromatography using a flame ionization detector. Chloride analysis of aqueous solutions was done by titration with mercuric nitrate.

5.6.2.4 Test Procedures

Tests were run following the basic procedure described in Section 3.2.

5.6.3 Test Results

Operating conditions for the four test runs are summarized in Table 5-21. The results of these tests are summarized in Tables 5-22 and 5-23.

TABLE 5-21. OPERATING CONDITIONS FOR WASTE DESTRUCTION TESTS AT THE 3M COMPANY FACILITY

Test ID Code and Description	3MI(B) (Fuel Oil Only)	3M2 (Fuel Oil Plus PVC Waste)	3M3 (Fuel Oil Plus PVC Waste)	3M4 (Fuel Oil Plus PVC Waste)
Primary Combustion Zone Temperature °C (°F)	870 (1600)	870 (1600)	870 (1600)	870 (1600)
Secondary Combustion Zone Temperature °C (°F)	1095 (2000)	1095 (2000)	980 (1800)	980 (1800)
Combustion Gas Detention Time (seconds)	3	3	3	2
Rotary Kiln Rotation Rate (rpm)	0.2	0.2	0.2	0.2
Waste Feed Rate				
(drums/hr)	6	6	6	6
(metric tons/hr)	0.845	0.845	0.845	0.845

TABLE 5-22. 3M RESULTS SUMMARY

	Background Test	Waste Tests		
Operating Conditions	3M1(B)	3M2	3M3	3M4
Primary Combustion Zone Temperature, °C (°F)	870 (1600)	870 (1600)	870 (1600)	870 (1600)
Secondary Combustion Zone Temperature, °C (°F)	1090 (2000)	1090 (2000)	980 (1800)	980 (1800)
Combustion Zone Gas Residence time, sec	3	3	3	2
Waste Feed Rate, Metric tons/hour		0.845	0.845	0.845
Quality of Combustion Gas				
Particulate, mg/m^3	122	427	357	378
Total Organics, mg/m^3	48	38	39	60
Chlorinated Organics, mg/m^3	--	<0.02	<0.02	<0.04
Hydrochloric Acids, mg/m^3	--	1660	1660	1485
Quality of Stack Gas				
Particulate, mg/m^3	40.2	--*	70.9	71.4
Hydrochloric Acid, mg/m^3	0.65	--*	14.5	10.3
Quality of Scrubber Water				
Total Organics, mg/ℓ	2.4	5.6	5.0	0
Hydrochloric Acid, mg/ℓ	15	414	719	816

*No stack sample was acquired during this test.

TABLE 5-23. QUANTITATIVE RESULTS OBTAINED FROM ON-LINE INSTRUMENTS

	Concentration *			
	3M1(B)	3M2	3M3	3M4
Volatile Hydrocarbons (as methane)	21 ppm	15 ppm	13 ppm	13 ppm
Carbon Monoxide	89 ppm	20 ppm	19 ppm	14 ppm
Carbon Dioxide	6.3%	7.0%	6.1%	6.3%
Oxygen	10.6%	11.2%	11.0%	11.4%
Nitrogen Oxide (NO)	38 ppm	74 ppm	24 ppm	29 ppm

*In the three waste tests, the on-line instruments showed periodic fluctuations corresponding to the batch feed method used. Values shown are means estimated by averaging individual data points at 1.5 minute intervals over a 30-min period during each test.

No vinyl chloride monomer was detected in the incinerator combustion zone effluent; the limit of detection was 0.2 ppm (v/v). The predominant organic species identified in the combustion zone effluents were polynuclear aromatic hydrocarbons at estimated concentrations of 2 to 5 mg/cu m. These species were found in the background (fuel oil) test as well as in the waste test samples, and are therefore not attributed uniquely to combustion of the PVC waste. Some members of the general class of polynuclear aromatic hydrocarbons are known to have high toxicity (e.g., benzo[a]pyrene - a carcinogen); however, those particular species were not the predominant polynuclear aromatics in these test samples.

Concentrations of hydrochloric acid in the combustion zone effluent were estimated at about 1.5 g/cu m. Stack emissions of hydrochloric acid were <15 mg/cu m. Total particulate emissions from the stack were >75 mg/cu m. There was no evidence from analyses of the solvent extracts of the scrubber water samples that any significant quantity of organic material was present.

5.6.4 Interpretation of Results

Waste destruction efficiencies, as measured by total quantities of chlorinated organics in the effluent, were estimated as greater than 99.995 percent in each of the three tests. The total destruction efficiencies were 99.80 to 99.88 percent. The data suggest that destruction was marginally less efficient when combustion zone gas residence time was reduced from three seconds (3M2 and 3M3) to two seconds (3M4).

The results confirm that PVC waste can be incinerated without formation of detectable quantities of vinyl chloride monomer (detection limits <0.2 ppm in combustor effluent). In fact, no species uniquely attributable to the PVC waste and known to be hazardous were found in the incinerator effluents. Certain potential adverse impacts can be attributed to the presence of polynuclear aromatic hydrocarbons in all four tests, including the background test with No. 2 fuel oil alone. These species are not uncommon in combustion process effluents.

The wet scrubber system was found to have >99% efficiency for removal of HCl. Particulate removal appeared to be somewhat less efficient (ca 80%).

Results of on-site analysis for vinyl chloride monomer during these tests suggested that thermal destruction of drummed PVC waste could be carried out without significant risk to operating personnel, provided that direct exposure to drum head space was precluded.

5.6.5 Waste Destruction Cost

Capital and operating cost estimates were prepared for a system of the size tested at 3M Company and for a much smaller system, i.e., one more nearly matching the requirements of an individual PVC manufacturing facility. (The 3M Company facility has a capacity which exceeds the estimated annual U.S. production of PVC waste similar to that tested.) In preparation of these estimates, it was assumed that soda ash, rather than ammonia, would be used for neutralization of wastewater. The basis for the cost estimates is given in Section 3.6. Table 5-24 summarizes the estimated capital and operating costs for the two sizes of PVC incineration system.

TABLE 5-24. CAPITAL INVESTMENT AND OPERATING COSTS FOR ROTARY HEARTH INCINERATION OF PVC WASTE

	Metric Tons/Year	
	6700	335
Estimated Capital Investment $ Millions	7.80	1.30
Operating Costs, $/Metric Ton		
Operating Labor	44.50	380.30
Auxiliary Fuel	185.60	185.60
Utilities, Chemicals, Freight	28.90	28.90
Maintenance	37.30	124.50
Capital Related Items	285.70	1047.70
Total Estimated Operating Cost	582.00	1767.00

5.7 ROLLINS FACILITY TESTS - ROTARY KILN INCINERATION OF PCB-CONTAINING CAPACITORS AND LIQUID INJECTION INCINERATION OF NITROCHLOROBENZENE WASTE

Rollins Environmental Services, Inc., is a contract disposal facility located in Deer Park, Texas. The Rollins incineration system, consisting of a rotary kiln and a liquid injection burner feeding a common afterburner, was selected as representative of full-scale waste destruction equipment presently in commercial use. Rotary kiln incineration represents a well-established technology with widespread applicability to a variety of hazardous wastes. Total heat release is 28 million kcal/hr, with combustion gas temperatures of 1300°C in the afterburner. Stack emissions are controlled by a venturi scrubber system.

The two wastes tested at the Rollins facility, PCB-containing capacitors and nitrochlorobenzene production waste, were initially selected on the basis of their suitability for destruction in a rotary kiln incinerator. A conveyor system was used to feed either hammermilled or whole capacitors into the kiln. The afterburner provided additional residence time at temperatures sufficient to insure efficient destruction of the PCB in the capacitors. NCB waste was selected to be burned in the kiln, but did not atomize properly by itself in the kiln burner nozzle at Rollins. After being mixed with No. 2 oil, the NCB was fed through the liquid injection burner which fires the afterburner. This, in effect, provided only a single stage of combustion for the NCB tests.

5.7.1 Process Description

The Rollins incineration facility process is shown schematically in Figure 5-7. Basic system components include:

- Rotary kiln incinerator
- Waste liquid burner
- Afterburner
- Waste feed systems
- Auxiliary fuel feed systems
- Instrumentation
- Emission control system

5.7.1.1 Incineration System

The incineration system consists of a rotary kiln and a liquid injection burner, both feeding a common afterburner. Maximum total heat release is 28 million kcal/hr. The kiln is 4.9 meters long and 3.2 meters in diameter. Flame temperature in the kiln is nominally 1300°C.

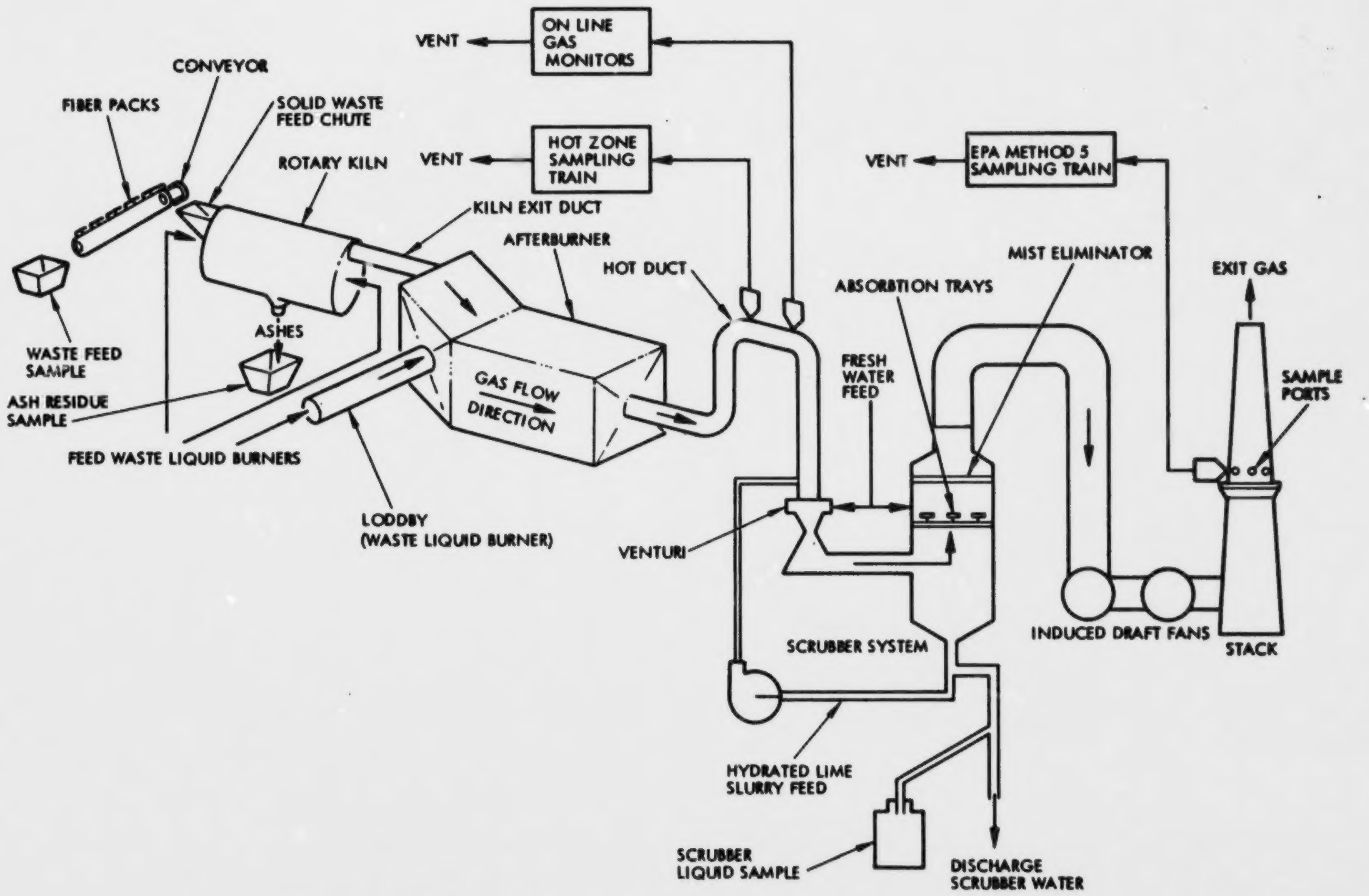
VENT
ON LINE GAS MONITORS
CONVEYOR
FIBER PACKS
SOLID WASTE FEED CHUTE
VENT
HOT ZONE SAMPLING TRAIN
ROTARY KILN
VENT
EPA METHOD 5 SAMPLING TRAIN
KILN EXIT DUCT
AFTERBURNER
HOT DUCT
MIST ELIMINATOR
EXIT GAS
ABSORBTION TRAYS
ASHES
WASTE FEED SAMPLE
GAS FLOW DIRECTION
FRESH WATER FEED
SAMPLE PORTS
ASH RESIDUE SAMPLE
FEED WASTE LIQUID BURNERS
LODDBY (WASTE LIQUID BURNER)
VENTURI
INDUCED DRAFT FANS
STACK
SCRUBBER SYSTEM
HYDRATED LIME SLURRY FEED
SCRUBBER LIQUID SAMPLE
DISCHARGE SCRUBBER WATER

Figure 5-7. Schematic of Rollins Environmental Services Incinerator

The waste liquid burner (Loddby) measures 4.9 meters in length by 1.6 meters diameter. Loddby flame temperature is approximately 1500°C. Resulting afterburner gas temperature is typically 1300°C. Afterburner dimensions are: 10.6 meters overall length, 4.0 meters high, and 4.3 meters wide. Overall retention time of the incineration system is from two to three seconds.

5.7.1.2 Waste and Fuel Feed Systems

Solid wastes, usually packed in fiber drums, are fed into the rotary kiln by a conveyor. Liquids and sludges may also be pumped into the kiln. Liquid wastes that can be burned in the Loddby are fed directly from tank trucks into the burner.

Both the kiln and the Loddby are equipped with natural gas ignitors and gas burners for initial refractory heat-up, flame stability, and supplemental heat, if necessary, Number 2 fuel oil was also used as auxiliary fuel for these tests. Fuel oil was used to provide heat for the PCB tests, since the capacitors by themselves did not have sufficient heat capacity. The nitrochlorobenzene waste was mixed with fuel oil in order to be fed into the Loddby for incineration.

5.7.1.3 Instrumentation

Measurements were made of all process parameters, including temperatures, pressures, and flow rates. The following operating temperatures (see Figure 3-1) were recorded during each test: 1) kiln flame, 2) kiln exit duct, 3) Loddby flame, 4) afterburner, and 5) hot duct. Measured flow rates included: 1) natural gas, 2) auxiliary fuel oil to the kiln burner, 3) auxiliary fuel to the Loddby burner, and 4) waste feed. In addition, scrubber venturi pressure drop and lime consumption were also monitored during tests.

5.7.1.4 Emission Control System

Atmospheric emissions from the combustion of solid and liquid wastes during the Rollins incineration tests were controlled by a venturi scrubber. Lime slurry is injected to neutralize the scrubber water. The neutralized scrubber water enters settling ponds where it is analyzed and further treated, if necessary, before discharge. Exhaust gases also pass through absorption trays and a mist eliminator before entering the stack. The exhaust stack is 30 meters high with standard sampling ports and a platform about 16 meters above ground level.

5.7.2 Test Description

5.7.2.1 Wastes Tested

PCB-Containing Capacitors

Polychlorinated biphenyls (PCBs) have been used extensively in capacitor dielectric fluids, with an estimated 11,000 metric tons per year produced for this use. Although other materials are now being used as substitutes for PCB, thousands of tons of capacitors, each containing 20 to 40 percent PCB by weight, are taken out of service annually due to failure or obsolescence. The PCB fluid drained from several capacitors similar to the ones tested was colorless and had a specific gravity of 1.4 at 15.6°C (60°F). The fluid would not ignite in a calorimeter, thus its heating value is estimated to be less than 3,000 kcal/kg (5,000 Btu/lb). Its elemental composition was approximately 55 percent carbon, 2.6 percent hydrogen, and 43 percent total halogens (as chlorine). Sulfur and nitrogen contents were 80 ppm and 190 ppm, respectively.

Of the capacitors selected for the test burns, a portion were hammermilled and a portion were kept to be burned whole. Since the hammermilling process helps to mix and composite the material, a sample of the hammermilled "fluff" was taken to be representative of the feed for both the fluff and the whole capacitor test. A 20 g portion of the representative (fluff) sample was determined to consist of 29 percent extractable organics, 32 percent nonextractable organics (e.g., paper and plastics), and 39 percent ash. The extractable organics were analyzed by GC/MS. This analysis found the extract to be virtually entirely PCB compounds, the approximate distribution of which is shown in Table 5-25.

TABLE 5-25. COMPOSITION OF PCB SAMPLE

	Estimated Concentration	
Compound	g PCB/kg Fluff	Percent of Total PCB Compounds
Monochlorobiphenyl	1.0	0.2
Dichlorobiphenyl	94	20
Trichlorobiphenyl	150	31
Tetrachlorobiphenyl	180	37
Pentachlorobiphenyl	55	11
Hexachlorobiphenyl	3.3	0.7

Nitrochlorobenzene (NCB) Waste

The principal use of the desired NCB product is as an intermediate material for the manufacture of synthetic dyes, drugs, pesticides, and photochemicals. The estimated total annual production of NCB waste similar to that selected for testing was 9100 metric tons (20 million lbs) in 1974.

An early survey sample of this waste was a black liquid containing crystalline material which was identified as p-nitrochlorobenzene. This sample had a heating value of 5,050 kcal/kg (9100 Btu/lb). The representative sample taken during the test burns was very similar in nature but appeared to lack the crystalline isomer. This sample had a density of 1.33 g/ml and an elemental composition of 46 percent carbon, 2.8 percent hydrogen, 8.9 percent nitrogen, 23 percent chlorine, and 0.02 percent sulfur.

Further analysis of the representative waste sample determined that it was 95 percent nitrochlorobenzene with the ortho isomer predominating. The remaining 5 percent was made up of dinitrochlorobenzene and nitrobenzene, as well as some compounds tentatively identified as styrene-substituted di-tolyethers.

The NCB waste contained 0.8 percent ash which was composed mainly of calcium, iron, and magnesium. No potentially hazardous metals were detected at levels above 1 ppm in the waste.

5.7.2.2 Sampling Methods

The sampling procedures used were those described in Section 3.3 with the following modifications:

- Reagents were added to both combustion zone and stack sampling trains in order to scrub hydrochloric acid from the gases. In addition, for the NCB tests larger volume impingers were needed to contain the required amount of reagent.
- Grab gas samples of the combustion zone effluent were collected from the bypass line of the hydrocarbon analyzer.
- For the NCB test, an empty impinger was used between the filter and the sorbent trap, to condense water.

Spent scrubber water samples were taken either from the aeration tank by compositing with a proportional sampling pump, over a three-hour period coincident with the combustion zone gas grab sample, or from the end of a drain pipe that carried the used scrubber water to treatment ponds. The well water being fed into the single pass wet scrubber was sampled from a pipe transporting the well water into the scrubber system.

The solid residues remaining after combustion of the PCB capacitor wastes in the rotary kiln were accumulated in a hopper below the kiln throughout each test. Samples were then taken from this collected residue at the end of each test. The residue (consisting of steel hoops from the fiber drums, large chunks of metal, fine ash, etc.) was nonhomogeneous in nature, thus a truly representative sample could not be obtained without the use of grinding and milling equipment.

5.7.2.3 Analysis Methods

Analytical methods used were those described in Section 3.3, with special effort given to analyses for PCBs in the collected samples.

5.7.2.4 Test Procedures

The PCB tests conducted at Rollins consisted of one test burn of waste capacitors that had been hammermilled and sealed in 130 liter (35 gallon) fiberpacks and one test burn of whole waste capacitors. Before each test burn, the kiln and Loddby were purged with a 1- to 2-hour burn of No. 2 oil. The waste was fed into the kiln either as whole drums of the hammermilled material or as individual capacitors. Target temperatures for the PCB tests were a kiln flame temperature of 1320°C and a Loddby flame temperature of 1480°C.

Due to problems encountered in burning the NCB waste alone in the kiln, the NCB was dissolved in diesel oil and this solution was fired through the Loddby burner. For the test where the NCB waste alone was burned in the kiln, the kiln and afterburner were preheated and purged by burning diesel fuel (in the kiln and Loddby burner) for one hour prior to the feeding of the NCB waste. For the tests where NCB waste was mixed with diesel fuel and fed to the Loddby burner, there was no diesel fuel purge of the kiln and Loddby burner prior to firing the waste, since there was no means readily available for feeding straight diesel oil to the Loddby burner. (The only available feed tank for the Loddby burner was filled with the diesel fuel/NCB mixture.) A one-hour "purge" period while feeding the oil/NCB blend was allowed prior to sampling.

5.7.3 Test Results

A summary of the test results is presented in Table 5-26, beginning with the range of test conditions for each waste, including combustion temperature, residence time, and waste feed rate. The summary presented in this table also covers analytical results from samples taken during testing, destruction efficiency calculations based on those results, and costs for commercial application of the Rollins incineration system. These areas are discussed further in the following sections.

5.7.3.1 Incinerator Operating Conditions

The feed rate of PCB capacitors during the test burns was 210 kg/hr hammermilled (330 kg/hr including the weight of the fiber drums) and 360 kg/hr whole with residence times of 3.2 and 3.0 seconds for the respective tests. Auxiliary fuels were fed at average rates of 2080 liters per hour of No. 2 oil and 89 cubic meters per hour of natural gas. The following average temperatures were achieved:

TABLE 5-26. ROLLINS RESULTS SUMMARY

	PCB-Containing Capacitors		Nitrochlorobenzene Waste	
	Hammermilled	Whole	1st Test	2nd Test
Kiln Flame Temperature (^{o}C)	1252	1339	Not Used	Not Used
Afterburner Temperature (^{o}C)	1331	1332	1307	1332
Calculated Residence Time (sec)	3.2	3.0	2.3	2.3
Solid Waste Feed (kg/hr)	2.0	360	None	None
Liquid Waste Feed (l/hr)	None	None	404	350
Number 2 Oil Feed (l/hr)	2411	2300	1616	1410
Quality of Stack Emissions:				
Particulate (mg/m^3)	35	53	14	16
Hydrochloric Acid (mg/m^3)	Not Analyzed	Not Analyzed	13	13
Trace Metals (mg/m^3)	2.7 Pb	3.3 Pb		
Quality of Combustion Gas:				
Total Organics (mg/m^3)	14	23	42	53
Waste Content (mg/m^3)	Not Detected (<0.005)	Not Detected (<0.005)	Not Detected (<0.05)	Not Detected (<0.05)
Trace Metals (mg/m^3)	12Pb,1.0Sn	11Pb,2.6Sn		
Quality of Scrubber Water:				
Total Organics (mg/l)	0.19	0.23	1.0	1.4
Trace Metals (mg/l)	1.7Pb,1.5Zn	4.0Pb,1.3Zn		
Chloride Ion (mg/l)	Not Analyzed	Not Analyzed	1725	1815
pH	5	5	3	3
Quality of Ash:				
Waste Content (mg/kg ash)	Not Detected (<0.1)	470	No Ash	No Ash
Destruction Efficiency:				
Total Organics (percent)	99.96	99.94	99.84	99.87
Waste Constituents (percent)	<99.999	99.5(a)	>99.999	>99.999

(a) Overall destruction efficiency reduced due to high waste content in ash. Efficiency based on combustion gas sampling was >99.999 percent.

	Hammermilled Capacitors	Whole Capacitors
Kiln Flame (^oC)	1252	1339
Kiln Duct (^oC)	488	493
Loddby Flame (^oC)	1499	1509
Afterburner (^oC)	1331	1332
Hot Duct (^oC)	1089	1096

After the failure of the NCB waste to burn satisfactorily in the rotary kiln on its first test, it was blended with No. 2 oil at a 4:1 volume ratio (20% NCB in the final blend) and fed through the Loddby burner. Feed rates were 2020 and 1760 liters per hour for the two subsequent test burns. During these tests, 250 and 390 liters/hr of No. 2 oil were also fed to the kiln in order to maintain temperatures, and natural gas consumption averaged 130 m^3/hr. Retention time for both NCB tests was 2.3 seconds. The following average temperatures were achieved:

	2nd NCB Test	3rd NCB Test
Loddby Flame (^oC)	1548	1510
Afterburner (^oC)	1307	1332
Hot Duct (^oC)	1075	995

Both background tests burned approximately 2100 liters/hr of No. 2 oil and maintained afterburner temperatures of 1290^o - 1310^{o}C with a residence time of 2.6 seconds.

5.7.3.2 Characterization of the Incineration Process

PCB-Continuing Capacitor Tests

The gas composition as measured by the on-line analyzers was fairly constant through the PCB test burns. During the hammermilled and whole capacitor tests, concentrations for oxygen averaged 9.8 and 10.1 percent and for carbon dioxide averaged 8.8 and 9.3 percent, respectively. Other gas concentrations were 5 to 10 ppm CO, 60 ppm NO, 35 to 40 ppm SO_2, 470 to 670 ppm HCl, and 7.5 percent H_2O.

Samples from the hot zone train were analyzed specifically for PCB compounds by GC/MS. No PCBs of any class were found in these samples at an overall detection limit of 5 micrograms per cubic meter. The amount of total organics found was 14 and 23 mg/m^3 for the No. 2 oil background test also. These organic materials were qualitatively determined to be primarily silicones, hydrocarbon oils and phthalates along with traces of several other nonhazardous organic compounds. The major inorganic elements found in the combustion zone samples from the PCB tests were boron, cadmium, copper, iron, potassium, phosphorus, lead, and tin. Major levels of aluminum may also have been present; however, the relatively high background of this element in the glass fiber filters makes that impossible to determine.

Particulate loadings in the stack were 35 and 53 mg/m^3 for the hammermilled and whole capacitor tests, respectively. The predominant elements found in the combustion gas were also the major inorganic constituents of the stack gas. Copper, iron, lead, phosphorus, tin, and cadmium were the major elements in the stack with cadmium being present at 0.3 mg/m^3, lead at 3 mg/m^3, and tin at 0.7 mg/m^3.

Analysis of extracts of the scrubber water samples found no PCBs above the detection limit of 0.01 mg/liter. No hazardous organic compounds other than PCBs were detected either. The scrubber waters showed noticeable increases in aluminum, copper, lead, and zinc though the concentrations of these metals in the effluents were still below 10 ppm.

Combustion of the PCB-containing capacitors produced appreciable amounts of solid residues from the rotary kiln. The two residue samples were quite similar in physical appearance except that the one from the hammermilled capacitor test was slightly reddish in color. PCBs were found in both residue samples. Only traces were found in the residue from the hammermilled capacitor test at a level estimated to be less than 1 ppm. However, relatively larger quantities (470 ppm) were found in the residue from the whole capacitor test. These PCBs from the residue were almost entirely tri-, tetra-, and pentachlorinated biphenyl compounds.

The major elements composing the residues were found to be aluminum, iron, silicon, copper, tin, phosphorus, lead, zinc, and possibly potassium, all of which are the same constituents found to have predominated in samples from other areas of the kiln system. Together, Al, Fe, and Si composed approximately 70 percent of the residue samples.

Nitrochlorobenzene Waste Tests

Results of the NCB tests are summarized in Table 5-26. The concentration of NCB itself in the combustor effluent gas was below detectable limits or 0.05 mg/cu m. The only chlorinated hydrocarbon identified was a species with molecular weight of 200 and an empirical formula of $C_{10}H_{13}O_2Cl$, at about 0.3 mg/cu m in the higher temperature NCB test effluent. Some high molecular weight nitrogen-containing compounds of unknown structure were found in the NCB test effluents; these appear to have been contaminants. The other organic species which were identified in all effluent gases include alkyl benzenes, benzoic acids and other oxygenated species that are normally expected products of combustion of aromatic materials (#2 diesel oil or NCB waste) and thus not of particular concern. Another species identified in samples from both NCB tests and the background test was dibutyl tin dichloride; this was apparently a residual from wastes burned by Rollins during the previous shift. Some species, such as silicones, were found and attributed to contamination.

Data obtained from the on-line instruments and gas-detector tube are presented in Table 5-27. Measurement of the hydrochloric acid content of the combustion zone effluent indicated a concentration about two times higher than the theoretical maximum based on chlorine content of the feed. The calculated maximum concentration was 2.5-3 g/m^3.

There was no evidence of any significant organic contamination of spent scrubber water. The chloride content of the spent scrubber water corresponded to that measured for the combustion zone effluent gas.

5.7.4 Interpretation of Results

Results of the waste destruction tests are summarized in Table 5-26. It should be noted that particulate stack emissions were higher for the whole capacitor test compared to the hammermilled capacitor test, and that metal concentrations in both stack and scrubber water effluents were, in general, slightly higher for the whole capacitor test which probably reflects the higher waste feed rate in that test.

Of significance also is the fact that while emissions of HCl from the incinerator alone were high (circa 6 g/m^3), the wet scrubber removed 99.8 percent of the HCl from the effluent and resulting stack emissions were approximately 13 mg/m^3.

No waste constituents were found in any of the combustion gas samples above the minimum detection limits. Incineration of each waste was accomplished with high effectiveness, with overall waste destruction efficiencies of over 99.999 percent for every test except incineration of whole capacitors, where waste residuals in the ash reduced the overall destruction efficiency to approximately 99.5 percent. The distribution of PCBs in this ash is significantly different from that of the waste feed material. The differing profiles indicate a much higher destruction efficiency for the lower chlorinated PCBs and a decreasing efficiency as the number of chlorine atoms per PCB molecule increases. No PCB concentrations above 0.1 mg/kg were found in the ash from destruction of hammermilled capacitors. Total organic destruction efficiencies ranged from 99.84 to 99.96 percent. In general, the capability of the Rollins incineration system to destroy either solid or liquid wastes was effectively demonstrated during these tests.

TABLE 5-27. CHARACTERIZATION OF COMBUSTION EFFLUENT FOR NCB TESTS

	R1(B)	R3	R4
	Concentration (volume basis)*		
On-Line Instruments			
Volatile Hydrocarbons	N.D.≠ <5 ppm	N.D. <5 ppm	N.D. <5 ppm
Carbon Monoxide	7 ppm	7 ppm	8 ppm
Carbon Dioxide	7.3%	7.0%	6.7%
Oxygen**	9.4%	9.7%	10.0%
Nitrous Oxide (NO)≠≠	50 ppm	170 ppm	165 ppm
Gas-Detector Tubes			
Chlorine	N.D. <1 ppm	N.D. <1 ppm	N.D. <1 ppm
Hydrochloric Acid	N.D. <2 ppm	N.D. <2 ppm	N.D. <2 ppm
Phosgene	N.D. <1 ppm	N.D. <1 ppm	N.D. <1 ppm
Sulfur Dioxide	10 ppm	12 ppm	15 ppm
Nitrogen Dioxide≠≠	-	>300 ppm	>300 ppm

*Wet gas basis

**Estimated from CO_2 concentration for R3 and R4

≠Not detectable

≠≠Due to instrument malfunction, the nitrogen dioxide concentration in the effluent could not be determined in these tests. About 2.5 g/cu m is the calculated maximum quantity based on the nitrogen content of the waste.

The calculated destruction efficiency based on total organic emissions was 99.94% for the background test; for the two NCB waste tests the corresponding values were 99.94% and 99.87%. The calculated destruction efficiencies based only on waste components were 99.999% for both waste tests. The organic species identified in the hot zone effluent during the NCB tests do not include any compounds that are known to be hazardous at the concentrations found in these tests. The only species identified in the hot zone effluent which would clearly require some form of emission control are hydrochloric acid and nitrogen oxides.

The scrubber system was found to have a hydrochloric acid removal efficiency of 99.8% for the two NCB waste tests. Reliable data could not be obtained during these tests to characterize the nitrogen oxide emissions from NCB combustion.

5.7.5 Incineration Costs

Capital and operating cost estimates were prepared for incinerator systems similar to the Rollins unit to destruct each of the two wastes. Estimated capital investment, not including land cost, for a facility to hammermill and incinerate 5000 metric tons of waste capacitors per year is $3.65 million, with the total fixed and variable operating costs equivalent to $741 per metric ton of waste destroyed. These costs are summarized in Table 5-28. Over $300 per ton of operating cost can be saved if a high heat content waste is utilized instead of Number 2 fuel oil to provide temperatures required to destroy the PCB. Using a waste to incinerate the capacitors would be the actual commercial destruction method; however, in order to more precisely analyze the PCB combustion products, a clean-burning fuel oil was used as auxiliary fuel for these tests.

TABLE 5-28. ESTIMATED CAPITAL INVESTMENT AND OPERATING COSTS FOR ROTARY KILN INCINERATION OF PCB/CAPACITOR WASTES

	5000 Metric Tons/Year
Estimated Capital Investment $	3,648,900
Operating Costs, $/metric ton	
Operating Labor	79.20
Auxiliary Fuel	307.00
Utilities, Chemicals, Freight	92.10
Maintenance	65.70
Capital Related Items	197.10
Total Estimated Operating Cost	741.00

Estimated operating cost for destruction of 4540 metric tons per year of NCB waste (one half of estimated total volume generated annually) in a central, contractor-owned facility such as Rollins is $242 per metric ton, including cost of transporting wastes. For this central facility, presumed to operate with NCB waste over a four-month period of each year, the estimated capital investment is $3.75 million; therefore, the pro rata capital investment for NCB destruction would be $1.25 million (one-third use of facility). For an on-site facility, scaled to a size adequate for destruction of 4540 metric tons per year of NCB waste only, the estimated capital investment is $2.82 million and the estimated operating cost is $283 per metric ton. Both of these costing approaches are summarized in Table 5-29.

TABLE 5-29. CAPITAL INVESTMENT AND OPERATING COSTS FOR LIQUID INJECTION INCINERATION OF NCB WASTES

	4540 Metric Tons	
	Per Year	Per 4 Months
Estimated Capital Investment $ millions	2.82	1.25*
Operating Costs, $/metric ton		
Operating Labor	46.00	29.10
Auxiliary Fuel	20.20	51.70
Utilities, Chemicals, Freight	18.10	62.10
Maintenance	31.00	24.80
Capital Related Items	167.70	74.30
Total Estimated Operating Cost	283.00	242.00

*Prorated cost for one-third time use of large facility.

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